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NRL Report 6294

# Adhesive Restorative Dental Materials

## A Literature Survey of Inorganic Polymers

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## ABSTRACT

[A new adhesive restorative dental material must meet rigid requirements.] These must be kept in mind in screening inorganic polymer systems reported in the literature; but since the available literature data are limited, only three requirements—toxicity, chemical stability, and ease of manipulation—were used in this evaluation.]

[The problem was approached by considering polymers according to the group number of the elements contained in the polymer backbone. The inorganic polymers were in turn grouped into three classes: Class 1, polymers having only one element in the polymer backbone; Class 2, polymers having two different elements in the backbone; and Class 3, polymers having three or more different elements in the backbone.]

Inorganic polymer systems which appear most promising for use as dental materials are the Class 2 polymers containing linear silicon-oxygen backbones and Class 2 polymers containing boron-phosphorus or phosphorus-nitrogen ring systems as moieties in the backbone.]

## PROBLEM STATUS

This is a final report on adhesive restorative dental materials for the National Institute of Dental Research.

## AUTHORIZATION

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## ADHESIVE RESTORATIVE DENTAL MATERIALS

### A LITERATURE SURVEY OF INORGANIC POLYMERS

#### I. INTRODUCTION

##### A. Background

The development of an adhesive restorative dental material would represent a major contribution to dental science. To encourage and expand research in the area of dental materials, the Dental Study Section of the National Institutes of Health sponsored a workshop under support by a grant from the National Institute of Dental Research at the Indiana University Medical Center, September 28-29, 1961. "The conference was unique in that it, for the first time, brought together scientists in the respective disciplines which would be involved in the development of an adhesive restorative material" (1). Subsequently, an Advisory Committee on Adhesive Restorative Dental Materials was appointed to promote investigation of tooth structure, surface phenomena, polymer chemistry, and test methods.

It was considered possible that the vast literature in the fields of organic polymers, inorganic polymers, and ceramics might reveal materials with properties conducive to use as suitable adhesive restorative dental materials. The Advisory Committee has recommended that support be made available for thorough literature surveys in the three materials fields mentioned above for screening possible systems for dental application. The present survey, pertaining to inorganic polymers, has been completed at the Naval Research Laboratory.

##### B. Requirements for Adhesive Dental Restorative Materials

Before beginning the survey, we were confronted with such questions as: What is the composition and geometry of the tooth surface? What are the requirements of a perfect adhesive restorative dental material? What properties should be considered the most important for initial screening of materials? What specific test methods are used to evaluate new dental materials? A booklet containing the answers to these questions and many more needed by the novice in the dental materials field is being prepared by the Advisory Committee and will be available in the near future (2). Since the booklet was not available at the time this report was written, the following requirements which a dental restorative material should exhibit were established. The requirements, listed in order of importance for screening purposes, are

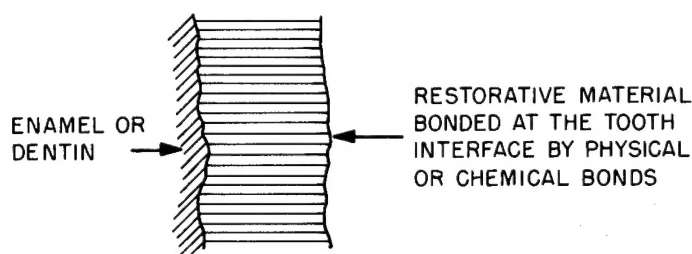
1. Nontoxicity
2. Resistance to chemical activity
3. Ease of manipulation
4. Adhesion to the cavity walls
5. Crush resistance
6. Resistance to abrasion
7. Thermal conductivity similar to enamel or tooth structure.



8. Coefficient of linear expansion similar to tooth enamel or tooth structure.
9. Harmonious color.

The desired material must cure rapidly in the mouth under moist conditions, without excessive heat evolution and with low shrinkage during cure. The resistance of the material to water, acids, and bases will be important initially; the long-range susceptibility to fungus and bacterial attack or pH changes in the mouth must be considered also. Although adhesion to the cavity wall directly or through an intermediary coating (Fig. 1) will determine the nature of the functional groups desired in a suitable material, the subject of adhesion will not be discussed in this report.

A. THROUGH PHYSICAL OR CHEMICAL BONDS



B. THROUGH INTERMEDIARY COATING

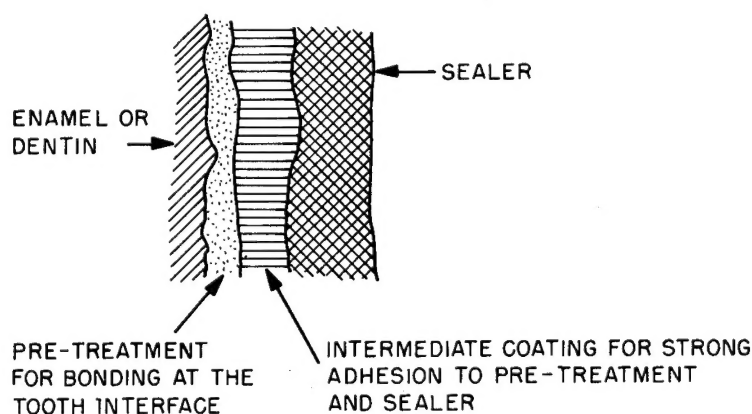


Fig. 1 - Adhesion to cavity wall

A perusal of the inorganic polymer literature reveals limited systematic evaluation of polymers having properties which make them suitable for dental application. An effort to systematize the evaluation of polymers was published by Adams, Bourke, Jackson, and Taylor (3). A compilation of specific tests needed to evaluate adhesive restorative dental materials is not yet available, although the booklet in preparation by the Advisory Committee (2) will contain recommended screening tests and procedures.

Evaluation of a polymer or polymer system based on all nine of the requirements listed above was not possible, because the literature pertaining to inorganic polymers

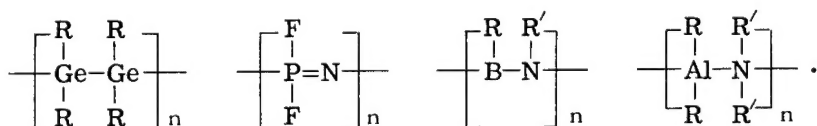
generally limited itself to reporting the existence, the preparation, structural data, and a multitude of possible patentable uses. Frequently, the only physical properties reported were the melting point, boiling point, and decomposition temperature. When a compound was reported to be "hydrolytically" stable or unstable, the method used to test the stability was seldom disclosed; comparison of stability data was impossible. Words such as "brittle," "hard," "flexible," and "plasticlike polymer" are but a few descriptive words found that have little meaning for screening purposes unless quantitative data are presented. To indicate broad classes of inorganic polymers for further evaluation, only the first three requirements listed above were considered; screening based on the remaining requirements must be sought by further investigation.

### C. Inorganic Polymers Defined

The definition and restrictions placed on the term inorganic polymer as used in this report must be considered, because the definition varies considerably from author to author (4,5). Inherent problems involved in specifying what constitutes an inorganic polymer have been discussed by Stone and Graham (4). In broad terms, an inorganic polymer is any substance containing a large number of repeated structural units, which involve elements other than carbon, connected by any type of chemical bond in any possible way. This unqualified definition of an inorganic macromolecule can be criticized as being too inclusive; the definition would cover all inorganic solids from quartz and glasses to the giant ionic crystals of inorganic salts. Flory (6) restricted the term polymer by introducing the concept of irregularity. Although chains or networks may exhibit a high degree of crosslinking, the number of units between points of crosslinking will vary greatly. Polymers may be prepared with high degrees of regularity, such as stereoregular and crystalline polymers; but the degree of ordered arrangement never approaches the almost perfect regularity exhibited by inorganic salts, for example quartz which is not considered a polymer in this report.

The inclusion of a degree of randomness to our unqualified definition of a polymer can be further implemented by considering that the interunit linkages or polymer backbone will not be seriously affected by physical processes such as melting or dissolving. Based on this restriction, inorganic salts and most polyatomic species in solution can be excluded from our discussion. Ceramics and glasses, substances which may fit our definition, will be excluded from our discussion because they are in areas which we feel deserve coverage by a separate literature survey. This report, then, will be limited to those substances which involve elements other than carbon connected by any type of chemical bond in any possible way to form interunit linkages or polymer backbones which will not be seriously affected by physical processes and which possess a degree of randomness in their molecular structure or physical state.

The inorganic polymers to be discussed will contain atom M linked to another atom L to form a repeating unit  $-(M-L)_n-$  where  $n$  is a relatively large number. The bonding between M and L may range from predominantly covalent to predominantly ionic and may include coordinate covalent bonding. Polymers which have complex organic groups as the link L, e.g., coordination polymers, will be excluded, but polymers with appended carbon derivatives which do not destroy the all inorganic backbone of the polymer will be included. The atoms M and L may be the same or different; one or all of the backbone atoms may have other atoms or groups of atoms attached to them, for example,



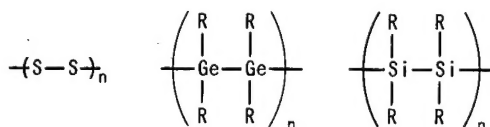
Inorganic polymers can be grouped into three classes: (a) polymers containing only one element in the backbone, (b) polymers containing two different elements in the backbone, and (c) polymers containing three or more different elements in the backbone. Table 1 lists examples of each of the three classes of inorganic polymers. Although an enormous number of element combinations seem possible, the combinations of elements forming inorganic polymers which are reported in the literature are relatively few. Oxygen and nitrogen are the most common linking elements L; complex organic ligands have recently opened a new field of "coordination" polymers, but as mentioned these will not be discussed in the present report. Interunit linkages are most numerous when oxygen is involved with other elements M. The elements M reported in the literature are few also; the most important elements considered in this report are silicon, phosphorus, boron, titanium, and aluminum. Table 2 lists the possible combinations between atoms M and L for the Class 1 and Class 2 polymers. Class 3 polymers may be derived from any combination, in varying amounts, of the units of Class 2 polymers.

#### D. General Characteristics of Inorganic Polymers

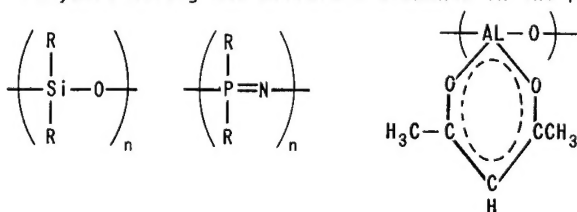
Two characteristics affect the formation of high-molecular-weight inorganic polymers: simple monomeric species are not isolable, and stable low-molecular-weight ring

Table 1  
Classes of Inorganic Polymers

Class 1: Polymers having only one element in the polymer backbone:



Class 2: Polymers having two different elements in the polymer backbone:



Class 3: Polymers having three or more different elements in the polymer backbone:

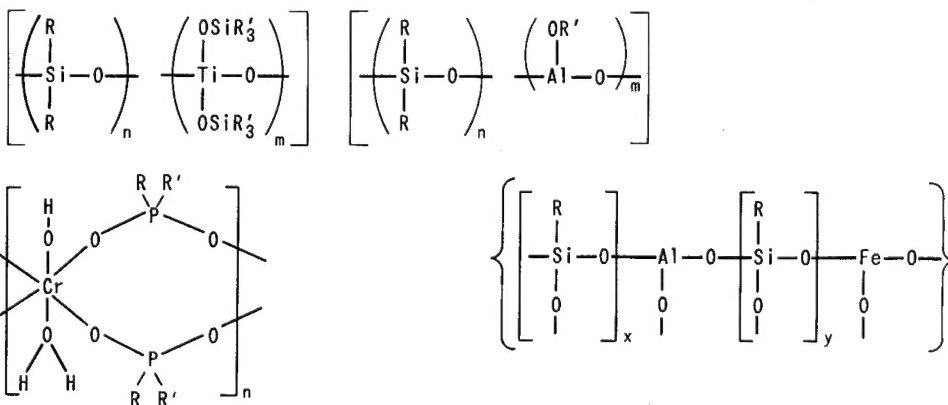


Table 2  
Important Combinations Which Form Inorganic Polymers  $\{M-L\}_n$

M†	L					
	M*	Oxygen	Nitrogen	Complex Organic Liquids	Carbon	Other Elements as designated
Group III						
B	✓	✓	✓		✓	P
Al		✓	✓	✓		
Group IV, IV B						
Si	✓	✓	✓		✓	
Ge	✓	✓			✓	
Sn	✓	✓		✓		
Pb		✓		✓		
Group V, V B						
P	✓	✓	✓		✓	
As	✓	✓	✓		✓	
Sb		✓	✓			
Group VI						
S	✓	✓	✓		✓	
Groups III A, IV A, V A VI A, V II A, VIII. For examples, Ti and other metals that form alkoxides and carboxylates		✓		✓		

\*Where  $M=L$ , class 1 polymers are formed.  $\{M-M\}_n$

Class 3 polymers will consist of two or more of the above units combined in the same polymer backbone.

†Von Antropoff's group designation used.

✓Element Combinations Investigated

compounds are easily formed by the condensation of the nonisolable monomers. Consequently, most inorganic polymers are formed by polycondensation which may involve heat, high pressure, or the liberation of undesirable products (7,8). The elimination of simple molecules during polycondensation might greatly affect the mechanical properties, porosity, and adhesive properties of the resulting polymers. The products of polycondensations are susceptible to excessive polymerization by crosslinking, and an early precipitation of the molecules from solution results before a reasonably high molecular weight is obtained. The cyclic low-molecular-weight polymers formed by condensations, solvolysis, or double decompositions can be re-formed to high-molecular-weight polymers under conditions, usually thermal, that cause ring rupture. Although most current methods of inorganic polymer preparation are not conducive to easy manipulation, the preparative methods alone should not negate the consideration of a polymer or polymer system as a possible dental material. The advances in polymerization mechanisms and techniques may alter the ease of manipulation so that polymers having excellent properties may be found practical as dental materials after investigation of new preparative methods.

Useful elastomers and resins contain long polymer chains capable of limited relative movement; the interchain movement will depend on the forces acting between the various polymer chains. Weak interchain forces are conducive to liquids or low-flow-point solids, while strong interchain forces produce brittle solids as in polymers crosslinked through bonds as strong as those in the polymer backbone. Inorganic substances such as silicates,

aluminates, and poly(titanates), which are brittle solids and insoluble in organic solvents suffer from excessive crosslinking in their rigid structures. To reduce interchain forces in synthetic inorganic substances, specific elements in the polymer backbone may be framed by organic groups. The properties of the resulting synthetic polymers differ sharply from the properties of the inorganic analogs. The framing groups can be used to regulate interchain forces and consequently interchain motion without complete chain separation. New synthetic polymers for dental applications should exhibit a degree of plasticity, and possibly be capable of solution in organic solvents from which films may be formed; these properties should be attainable by the proper choice of framing groups.

The use of organic groups appended to the elements M (Table 2) makes it possible to vary the properties of polymer systems within wide limits. The best example, as well as the most widely studied, is that of the silicon-oxygen polymer systems. Quartz,  $\text{SiO}_2$  (Fig. 2A), is a giant covalent macromolecule which is highly crosslinked, three dimensional, and rigid. Organic groups R incorporated into polymer structures via the silicon atoms in the polymer backbone, reduce the degree of crosslinking and form structures with (a) controlled two-dimensional crosslinking (Fig. 2B), (b) no crosslinking as in the linear structure (Fig. 2C), or (c) chain stoppers in controlled polymerizations (Fig. 2D). Extension of controlled crosslinking to other inorganic polymer systems provides a means to modify the polymer systems to produce compounds ranging from liquids to soluble rigid solids which are quite different from highly crosslinked structures. In polymers where an appended organic group involves an unstable metal-carbon linkage, the  $\text{R}_3\text{SiO}$  group has found extensive use as a blocking or framing group. If organic groups are appended to a given backbone structure, the general polar properties associated with inorganic polymers which make them promising as adhesive restorative dental materials will decrease as the organic character of the polymer increases. In some cases resistance to chemical attack, a problem associated with many inorganic polymers when moisture is present, can be modified by the addition of organic groups. Proper appendages to the polymer backbone afford the possibility of a wide range of tailor-made polymer properties.

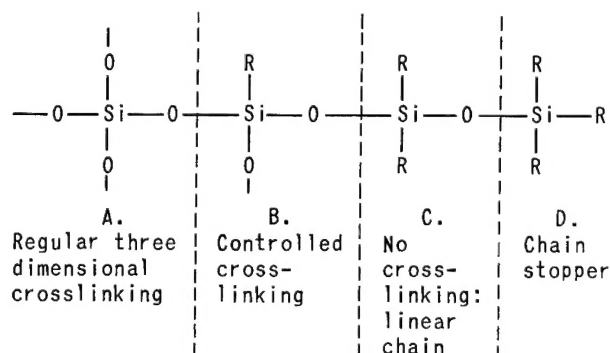


Fig. 2 - Control of crosslinking by appendant organic groups R

#### E. Trends in Inorganic Polymer Research

Through the years, the concern for high-temperature materials has led chemists to think of the marked thermal stability of inorganic oxides, for example, silicates and aluminates. Unfortunately, these materials lack the properties of the organic polymers which make the latter easy to fabricate into desired products. Convinced that highly polar bonding would solve the high-temperature stability problem, the inorganic polymer researcher has emphasized high-temperature uses under conditions of outer space, for example, temperature extremes, low pressures, and absence of moisture. Little research

has been directed toward polymers which may be useful under other conditions. The need for polar, chemically stable polymers, with specific thermal and mechanical properties not exhibited by organic polymers, is illustrated by the need for polymers or other materials which have suitable dental material properties. Presently known organic polymers are likely to be unsuitable for adhesive restorative dental materials because of the large differences in the coefficients of thermal expansion between the tooth and polymer. A second look at the many reported inorganic polymers which may have been only a curiosity in the past is required to uncover polymers and polymer properties which may not have been considered important at the time of reporting.

The available literature on inorganic polymers has now grown vast and complex. The increased interest in inorganic polymers is indicated by the numerous reference books, review articles, symposia, and conferences that have appeared during the last few years. The more recent books (9-12) and reviews (13-21) should be consulted for more general and comprehensive information than will be contained in this report.

#### F. Objectives of the Survey

The purpose of our study was to screen the available inorganic polymer literature for materials which appear promising as adhesive dental restorative materials, to direct the attention of those working in the field of inorganic polymers to the possible applicability of such materials to adhesive restorative dental material, and to recommend given areas of investigation that would be most fruitful for future investigations. Although it was not possible to state that a given polymer would be best for use as adhesive dental restorative materials, it was possible to consider several polymer systems which appear to be promising for further investigation and evaluation.

## II. LITERATURE SURVEY OF INORGANIC POLYMERS

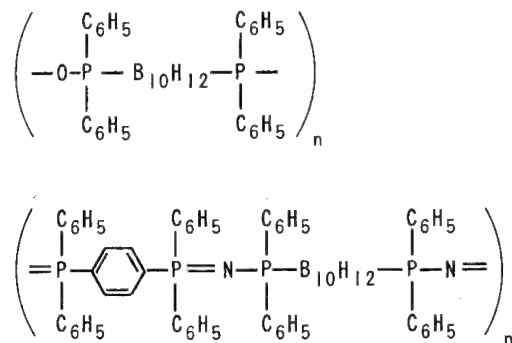
The inorganic polymer systems and polymer classes will be discussed according to the sequence presented in Table 2. A brief summary of the characteristics of each system will be presented. For those systems which are promising as adhesive restorative dental materials, representative polymers will be included with pertinent literature references.

### A. Group III: Boron and Aluminum

#### 1. Boron Polymers

The Class 1 polymers of boron, the boron hydrides and derivatives, have been the object of an enormous amount of investigation primarily because of the presence of the intriguing electron-deficient bonds. The boron hydrides are easily hydrolyzed with the evolution of hydrogen, the ease of hydrolysis decreasing with increasing molecular weight of the hydrides. Although a polymer approaching the composition  $(BH)_n$ , containing approximately 3 mole percent of amine, is only slightly affected by aqueous acids or bases (22), Class 1 boron polymers do not appear to be suitable for dental materials because of their chemical instability and mode of preparation. Recently, however, two anions,  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$  (23,24), were reported to exhibit remarkable thermal and chemical stability. It was noted that important polymeric materials might be realized if the polyhedral  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$  units could be directly linked together to form high-molecular-weight polymers containing boron-boron bonds.

The direct linking together of the open polyhedral structure of decaborane (Fig. 3) has not yet been accomplished. Two polymers containing the decaborane moiety in the polymer backbone have been reported (25,26):



The strong bonding between boron and phosphorus atoms has been utilized to incorporate the  $-\text{B}_{10}\text{H}_{12}-$  units into the backbone of the new inorganic polymers. Both polymers have relatively high molecular weights and a high degree of thermal stability. Although chemical stability was not reported, the polymers may suffer from a lack of hydrolytic and oxidative stability.

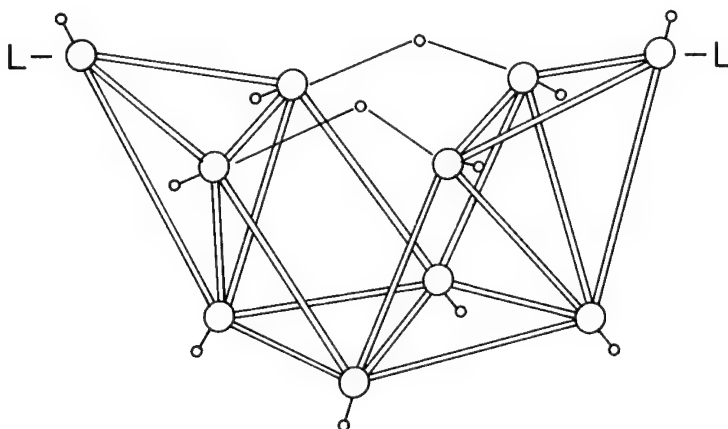
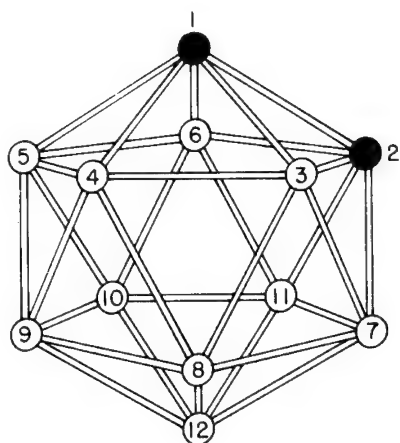


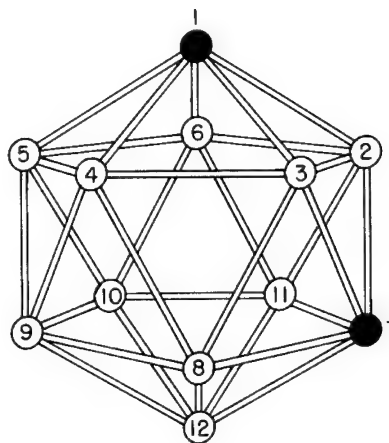
Fig. 3 - Open polyhedral structure of decaborane,  $\text{B}_{10}\text{H}_{12}\text{L}_2$

The study of decaborane chemistry revealed the formation of a new series of extremely stable organoborane compounds through the transformation of the open polyhedral structure of decaborane to an icosahedron in which two carbon atoms and ten boron atoms form a cage (Fig. 4) (27-40). The structure and chemistry of the new compound, dicarbaclovododecaborane(33) or carborane, and its derivatives are beyond the scope of this report. A summary of pertinent information has been published (41). From the definition of inorganic polymers stated in section IC, polymers containing the carborane unit  $-\text{B}_{10}\text{H}_{10}\text{C}_2-$  (Fig. 4A) should not be considered in this report. However, the use of the cage-like icosahedron structure to regulate the properties of other inorganic polymers by acting as a crosslinking agent, flexible link, or a stabilizing agent requires that some of the more important properties of the carborane derivatives be summarized.





A.  
Carborane



B.  
Neocarborane

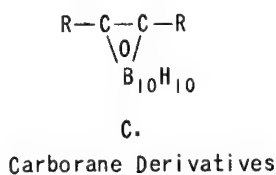
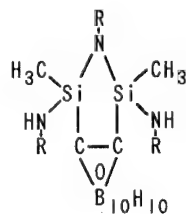
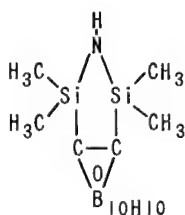
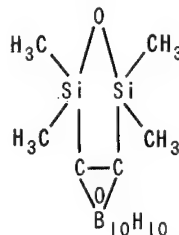
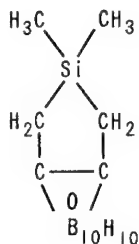
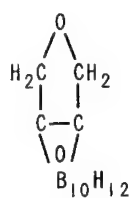


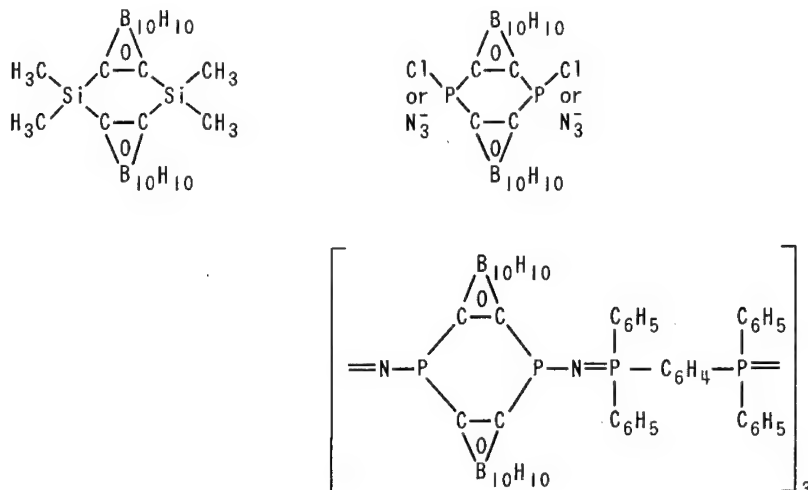
Fig. 4 - Organoborane compounds

The carborane derivatives are quite stable in comparison with other boron hydride derivatives. Not only is carborane stable at elevated temperatures, but the carborane nucleus is inert to air, moisture, and aqueous acids and alkalis. Some derivatives have been distilled unchanged from concentrated sulfuric acid (27,32,34). The chemistry of carborane and its derivatives supports a strong electron-withdrawing character for the polyhedron (29,34).

The formation of stable five-membered rings involving the two carbons in the icosahedron prevents straightforward formation of polymeric materials (29-31):



From the experimental evidence reported, the bond angles and bond distances of the two carborane carbon atoms are suggested to be of a magnitude particularly suited for participation in five-membered rings (30). Another preferred ring structure obtained during attempts to form linear polymers is a six-membered ring containing two sets of carborane carbon atoms (30,31,38):



Neocarborane (Fig. 4B), which no longer has carbon atoms adjacent to each other, has an entirely different chemistry than carborane (36,37). Neocarborane derivatives are less polar, more stable, more volatile, and slightly less dense than the corresponding carborane isomers. Only noncyclic derivatives are formed, thereby increasing the possibility of polymer formation without small ring formation. The neocarborane nucleus appears to be less electron-withdrawing and more stable to attack by amines than the corresponding carborane derivatives.

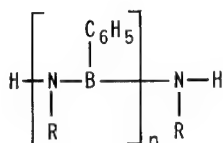
As more knowledge of the chemistry of the carboranes and neocarboranes is unfolded, useful dental materials containing the stable, bulky electron-withdrawing units may result. The sluggish reactions and the ease of stable ring formation of the carboranes may thwart efforts to easily prepare linear polymers. To date, only carborane polymers used as binders in preparation of high-temperature stable composites with asbestos have shown promise (42). Organic polymers modified by the inclusion of the carborane moiety in the polymer chain have been reported (43-45).

Compounds containing three-coordinated boron adjacent to an atom having a lone pair of electrons, for examples, nitrogen, oxygen, sulfur, and the halogens, are almost invariably readily hydrolyzed, frequently by brief exposure to the atmosphere. Thus, Class 2 polymers containing boron-nitrogen (46-48) or boron-oxygen (46,49) bonds may not be suitable as dental materials. Furthermore, most of the polymers based on completely inorganic boron-nitrogen and boron-oxygen chains are intractable and insoluble in organic solvents (50).

Planar (hexagonal or "white graphite") and tetrahedral (cubic or "diamond") forms of boron nitride, BN, are highly stable. The tetrahedral form, called borazon, is not attacked by common mineral acids, is only slowly oxidized in the atmosphere at 2000°C, is a good electrical insulator, and is hard enough to scratch diamond (51-53). The highly rigid material would be an impractical dental material. Attempts to introduce flexibility, elasticity, and workability into the highly stable boron nitride structures by forming

proper linear derivatives have been unsuccessful. The failure may be attributed to the tendency of the long-chain boron-nitrogen polymers to break down to six-membered rings, i.e., borazine derivatives; presumably the six-membered rings have a much lower energy state than the linear chains (46).

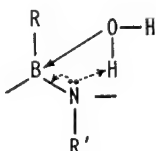
Several interesting approaches to the formation of linear boron-nitrogen polymers have been reported. One of these is to use bulky groups on the boron or nitrogen to sterically inhibit ring formation. One such postulated chain polycondensation has been reported by Gerrard (54):



where R = n-butyl,  $n \approx 40$

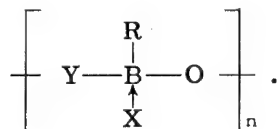
where R = isobutyl,  $n \approx 20$

The solids were reported to be easily hydrolyzed in boiling water. The investigation pertaining to the prevention of hydrolysis by proper choice of appended groups on nitrogen and boron does not show a simple correlation between the ease of hydrolysis and electron density on boron. Assuming a four-center transition state for hydrolysis,



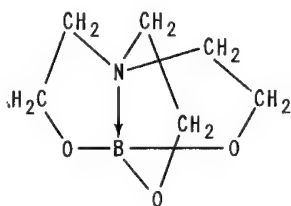
Gerrard (54) showed that some order does begin to appear between the ease of hydrolysis and electron density on boron. In general, acyclic boron-nitrogen compounds are more easily hydrolyzed, even by atmospheric moisture, than cyclic boron-nitrogen compounds. The location of appended groups on the ring nitrogen and boron is also important; N-triphenyl-B-trimethylborazine is unaffected by boiling water during an hour's reflux, but N-trimethyl-B-triphenylborazine is 90% hydrolyzed under the same conditions. A decrease in the nucleophilic character of nitrogen and a decrease in the electrophilic character of the boron appears to favor hydrolytic stability.

The occupation of the vacant p orbitals of boron by forming four-coordinated boron, for example by coordination, does not always materially reduce hydrolysis, but in several examples increased stability toward hydrolytic attack has been reported. The formation of a complete octet of electrons about the boron by formation of a donor-acceptor bond has been suggested by Rau (55) for the preparation of hydrolytically stable polymers of the type

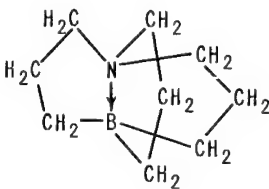


A bifunctional organic group Y is used to link together boron-oxygen units; a donor group X coordinated to boron is used to prevent attack by other agents and to prevent cross-linking without hindering polymerization. Unfortunately, introduction of coordination groups to increase the hydrolytic stability of a polymer was not always successful, although several examples of simple molecules indicated that the principle should be successful (56-58).

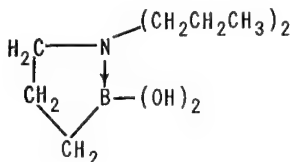
Boron esters are extremely sensitive toward both atmospheric oxidation and hydrolytic cleavage, while amino-alcohol esters, for example triethanolamine borate, possess an unusual degree of stability with respect to these influences. Based on the investigation of acidic degradation, Zimmerman (57) concluded that the resistance of triethanolamine borate to acidic degradation may be attributable to the presence of a nitrogen-boron dative bond



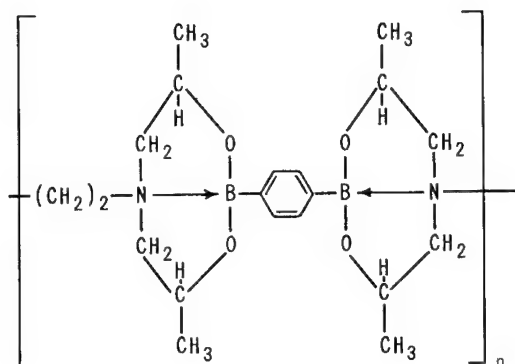
rather than to a steric hindrance effect. Another recently reported example, 1-aza-5-boratricyclo[3,3,3,0]undecane (58),



is soluble in organic solvents, stable in air and toward peroxidic oxidizing agents, and only slightly hydrolyzed when steam distilled. The acid obtained by the hydrolysis

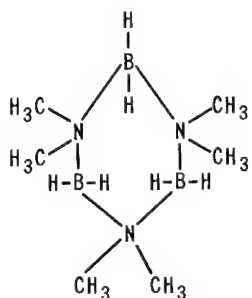


is further hydrolyzed with boiling aqueous potassium hydroxide only after 24 hours. The proposed dissociation of a boron-nitrogen bond at 100°C may activate the hydrolytic fission of the boron-carbon bonds. The principle of forming fully occupied p boron orbitals may lead to hydrolytically stable inorganic boron polymers. Although they are not considered as inorganic polymers in this report, polyesters of diboronic acids have been prepared in which the coordination principle is used to form hydrolytically stable polymers (59):

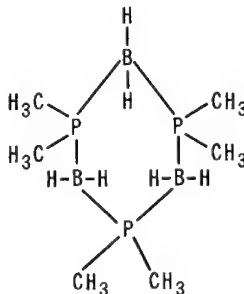


The polymer was recovered unchanged after 4 hours in boiling water.

The stabilizing effect of four-coordinated boron is also exhibited by dimethylaminoborane trimer (A) (22,60-62) and dimethylphosphinoborane trimer (B) (62,63):



A.

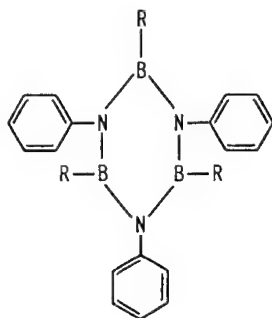


B.

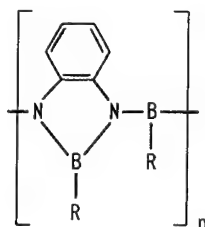
The trimeric, as well as the tetrameric, dimethylphosphinoborane reacts only slowly with concentrated hydrochloric acid at 300°C. The higher-molecular-weight dimethylphosphinoborane chain polymers are unstable toward heat compared to the cyclic trimer and tetramer. Somewhat less stable relative to phosphinoborane, dimethylaminoborane is inert toward water, acid, and methanol at room temperature; many hours of heating are required for the analytical breakdown by acid methanolysis. Proposed explanations of the increased stability of these compounds are discussed in the references cited.

Lappert (64-67) is studying the theoretical aspects of  $\pi$  bonding and restricted rotation of atoms involved in the backbone of linear boron polymers. A better understanding of the problems associated with forming linear, hydrolytically stable boron polymers may result from this research.

McCloskey et al. (50, 68-70) have approached the problem of linear polymer formation in a unique manner. If every two consecutive nitrogen atoms in a  $\text{-(B-N)-}_n$  system could be bonded to the same benzene ring, rather than to separate ones as in N-triphenyl-B-trialkyl(aryl)borazine,



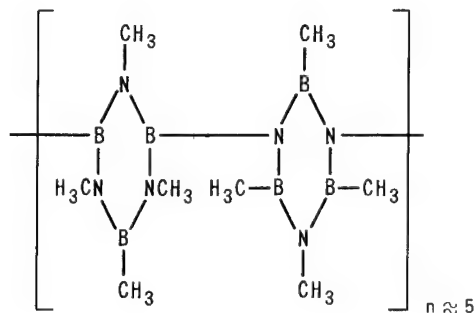
a stable five-membered ring system would be formed and a linear boron-nitrogen chain



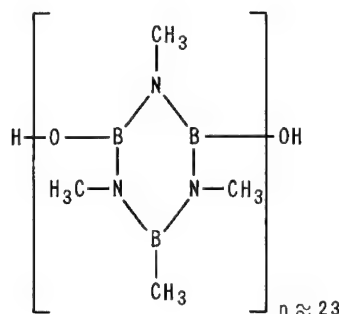
would be the most likely resultant configuration. Where R's were  $C_6H_5$  - the only materials reported were low-molecular-weight compounds which were soluble in benzene, slowly decomposed by water, and possibly decomposed by methanol.

Since the hydrolytic stability of cyclic boron-nitrogen compounds is greater than that of the acyclic compounds (48,71), polymer chains containing the stable ring moieties are suggested. McCloskey et al. (72a) have studied the "homoresinification" by pyrolytic dealkylation and dehydrogenation of various borazines between  $350^\circ$  and  $400^\circ C$ . Materials ranging from glasses to brittle resins were obtained with indication of polymerization through ring-attached alkyl groups. "Coresinifications" of borazine mixtures yielded interesting resins, especially when one borazole contained nitrogen-hydrogen bonds. All of the resins were isolated in very small yields after the high-temperature pyrolysis.

Wagner and Bradford (73) investigated two alternate means of effecting condensation polymerization of selected borazine derivatives: (a) lithium chloride elimination and (b) dehydrohalogenation. A low-molecular-weight resin, which contained boron-nitrogen ring linkages,

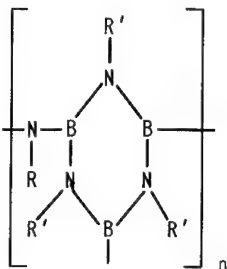


was obtained by the first method in about 96% yield. The hydrolytic stability of the compound was not indicated. The second method of linking rings appears applicable to formation of dental materials although details of hydrolytic stability of the resulting polymers were not reported. The hydrolysis of tetramethyl-B-dichloroborazine in the presence of triethylamine yielded a light brown glass with a degree of polymerization of approximately 23:

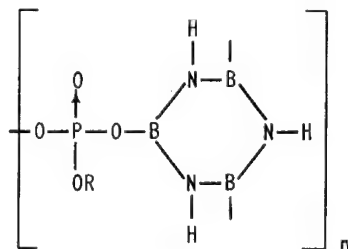


Although the boron-oxygen linkage between rings could produce polymers of poor stability toward acid and base attack, further investigation of the above-mentioned methods of linking rings may lead to useful dental materials.

The polycondensation of B-alkylaminoborazines by the elimination of primary amines is another means of linking borazine rings together; the polymers formed are solids which are highly crosslinked, insoluble in the usual organic solvents, readily hydrolyzed by water, and smell of amine in moist air (74,75):



When heated at 200°C at 0.5 torr, B-tris(dialkylphosphoryl)borazines undergo polycondensation with the elimination of trialkyl phosphate; the isolated polymers had properties indicative of borazine nuclei linked together by an alkoxyphosphoryl unit (74,76):



The polymers are reported to be insoluble in common organic solvents and only slowly hydrolyzed by boiling water.



Polymers formed by linking the borazine rings together through carbon atoms will not be considered in this report. The results obtained with the carborane moieties linked in polymers appear to be more suitable for dental materials than the use of borazine units.

A major disadvantage of boron-nitrogen polymers is that polymerization is generally initiated thermally. The polycondensation, generally accompanied by evolution of hydrogen, may produce end products of high hydrolytic stability (22,72b,74,77-79); however, the materials do not appear to have properties suitable for dental materials. For example, a chain polymer that was amorphous, insoluble, and stable to hydrolysis was reportedly formed when dimeric dimethylaminoborane,  $[(CH_3)_2NBH_2]_2$ , was heated at 150°C at 3000 atmospheres pressure (80). Unfortunately, the resulting polymer was not thermodynamically stable even at room temperature; it reverted to the dimer after a few months at room temperature.

Other Class 2 polymers of boron include the boron-phosphorus (62,63), boron-arsenic (62,81,82), boron-antimony (62), boron-sulfur (49,83,84), and boron-oxygen (49,55) systems. For further investigation as dental materials, only the boron-phosphorus system appears to show promise. McCloskey (85) has listed several boron-phosphorus polymers and their polymeric character. The phosphinoborines,  $[R_2PBH_2]_n$ , which have four-coordinated boron and phosphorus atoms (see discussion page 13), have unusual resistance to thermal, oxidative, and hydrolytic attack. As stated previously, the trimer and tetramer are thermodynamically more stable than the linear polymers (59,86,87). The addition of a basic end group coordinated to the boron atom of dimethylphosphinoborine monomer,  $(R_2PBH_2 \cdot NR_3)$ , suppresses the formation of the cyclic trimeric and tetrameric phosphinoborines (87). Hydrolytic-stability tests at 200°C did not show a clear correlation between end groups and the stability of various dimethylphosphinoborine linear polymers. Yolles (88) noted that polymers which have phosphorus-hydrogen bonds become water sensitive on standing, probably due to oxidation occurring at the phosphorus atoms. As noted in the case of the boron-nitrogen polymers, the thermal polycondensations currently used in the preparation of polyphosphinoborines would not make the system useful as dental materials at present; new techniques for effecting the polymerizations are needed.

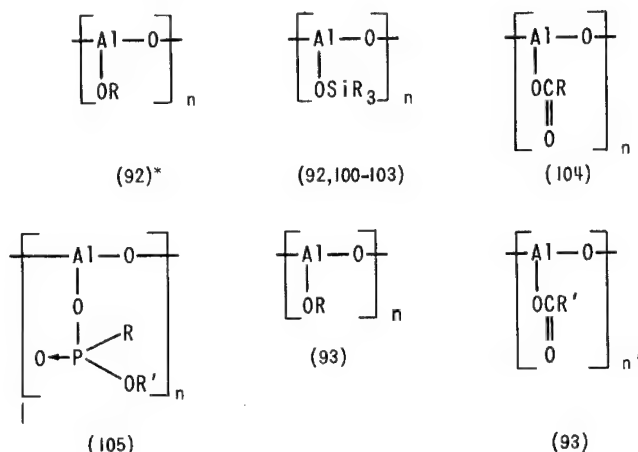
The last topic in this section is concerned with the Class 3 polymers of boron. The boron-oxygen-carbon systems, formed by reactions of boronic acids,  $RB(OH)_2$ , and glycols or diamines produce resins which are either water sensitive or of low molecular weight (89). In general, the polymers containing boron-oxygen-silicon units are sensitive to hydrolysis. When the silicon-to-boron ratio was 1:2, the materials obtained were curable to hydrolytically stable elastomers which exhibited self-adhesion properties (91). The poly(borosiloxanes) will be discussed further in the silicon section (section II,B1).

## 2. Aluminum Polymers

Class 1 aluminum polymers are not known. For consideration as dental materials, the Class 2 polymers of aluminum containing aluminum-oxygen or aluminum-nitrogen units in the polymer backbone are not expected to exhibit the necessary stability toward water, acids, and bases. However, the aluminum polymers will be briefly discussed because several facts reported will be instructive for future synthesis of inorganic polymers.

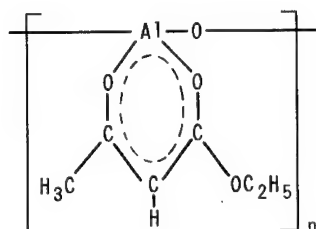
Polymeric materials containing aluminum-oxygen backbones are readily obtained by the reaction of aluminum alkoxides with water, organic acids, organic amides, or organic diols (92). The resulting polymers, ranging from gums to hard brittle solids, have been suggested for use as lubricants, fuel additives, water repellents, crosslinking agents, driers, and gelling agents; the polymers have been reported valuable in the production of resins, rubbers, paints, varnishes, lacquers, linoleum, ink, etc. (93-99). One structure

proposed for these polymers is a chainlike aluminum-oxygen backbone with substituent groups on the three-coordinated aluminum:

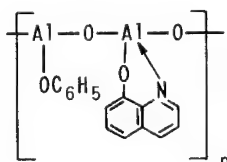


Crain and Koenig (106) proposed that the above polymers are highly crosslinked and not linear as shown; aluminum in the polymers is assumed to be four-coordinated. Rinse (99) suggests that a cyclic structure may be involved.

Efforts to increase the hydrolytic stability of the aluminum-oxygen system have been directed toward the formation of chelated four-coordinated aluminum in the polymer chain. Kugler (107) has prepared polymers which were solid, friable "aluminum resins" containing ethylacetoacetate-aluminum chelate rings in the polymer backbone:



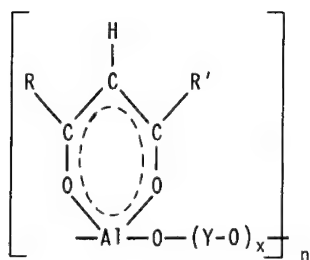
No direct mention was made concerning stability toward acids and bases, but an increased hydrolytic stability was indicated. McCloskey et al. (108) reported a mixed phenoxy/quinoline-8-oxy yellow solid polymer of molecular weight 2000 to 3000:



The hydrolytic stability was not reported, but the polymer may be expected to be attacked by acid or base.

\*Numbers in parentheses in this and subsequent drawings are reference numbers.

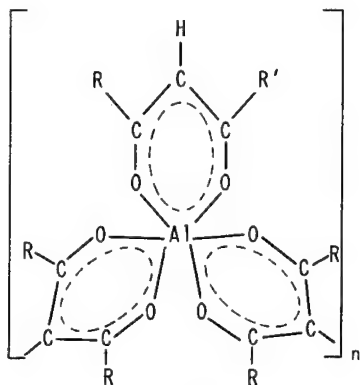
Patterson et al. (109) studied polymers containing chelated aluminum linked in the polymer chains through diols. Two types of structures were investigated; it was found that type I polymers exhibited hydrolytic instability



where Y is a diol; for example,  
butanediol-1,4

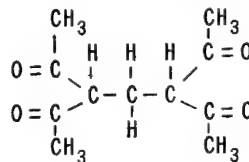
Type I

whereas polymers of type II were unchanged by prolonged suspension in water at 25°C.



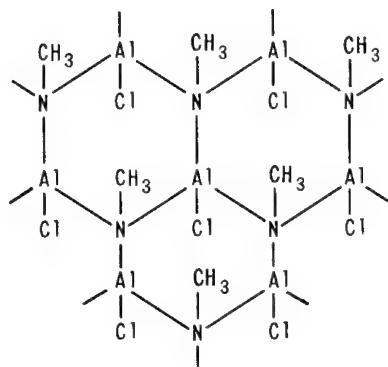
Type II

Example of chelating agent used:  
1,1,3,3-tetraacetylpropane,

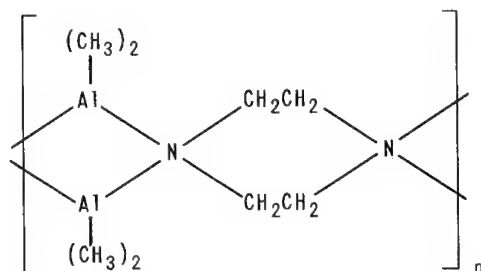


In boiling water, the type II polymers slowly formed gelatinous white precipitates. The six-coordinated aluminum proposed by structure II may explain the increased hydrolytic stability. It should be noted that the aluminum atoms in the proposed structure are no longer linked directly through oxygen, i.e.,  $(-Al-O-Al-)$ . To increase metal-oxygen and metal-nitrogen bond stabilities toward hydrolysis, organic groups have been used to bridge unstable inorganic repeating units; the procedure will be evident throughout this report.

In general, Class 2 aluminum-nitrogen polymers are hydrolytically unstable and readily dissolve in acids or bases. An interesting system studied by Laubengayer (110,111),  $(CH_3N-Al-Cl)_n$ , was a white, organic-solvent insoluble solid that reacted slowly but completely with water and dissolved readily in dilute mineral acids or alkalis. The proposed structure contains both four-coordinated aluminum and nitrogen

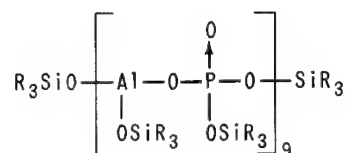
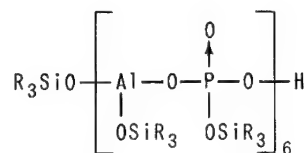


and is consistent with the insoluble, nonvolatile, and amorphous nature of the polymer. Crain and Koenig (106) prepared a polymer with aluminum-nitrogen units linked through an intermediate organic group, and the polymer exhibited an increased water stability:



The polymer, which was prepared by the reaction of trimethyl aluminum and piperazine, was unreactive toward water but decomposed in air at temperatures above 200°C. It is actually a Class 3 polymer, since it contains aluminum-nitrogen-carbon repeating units.

Other Class 3 polymers investigated are the aluminum-oxygen-phosphorus (101,112) and aluminum-oxygen-silicon (113) systems. The framing group  $R_3SiO$ , has been used extensively by Andrianov and co-workers in the study of the Class 3 aluminum polymers because of the chemical instability of the aluminum-carbon bond. Examples of the framing technique employed by Andrianov et al. (101,112) are:



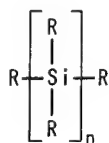
The Class 3 polymers containing aluminum-oxygen-silicon chains will be briefly discussed in the silicon section. Unfortunately, like the other aluminum polymers, the desired chemical stability is lacking, so that further consideration of these materials as dental material candidates is not warranted at this time.


## B. Group IV: Silicon, Germanium, Tin, and Lead

### 1. Silicon Polymers

The voluminous literature pertaining to silicon polymers indicates the extensive effort directed to finding industrially useful silicon polymers; the successes are evident by the numerous commercial silicon products. For a more detailed discussion than can be considered within the scope of this report, the reader should consult the recent review articles and books on silicon polymers (114-127). The scant mention of physical properties made it impossible to screen the available literature for individual silicon polymers; however, researchers actively engaged in silicon investigations may have knowledge of available materials which have the desired properties (see section IB) of dental restorative material. Our discussion of silicon polymers will be limited to general characteristics of the three silicon polymer classes and to general means by which silicon polymers may be altered to form useful dental materials.

Class 1 silicon polymers which contain silicon-silicon units in the polymer backbone are low-molecular-weight materials and relatively sensitive to chemical attack (124). Polymers containing organic groups on the silicon atoms

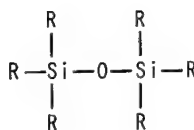
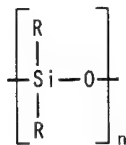
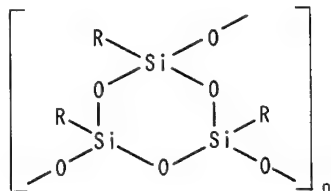
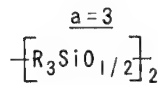
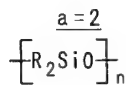
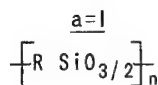
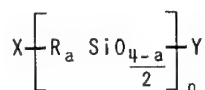


R may be H; CH<sub>3</sub>-; CH<sub>3</sub>CH<sub>2</sub>-; CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-; CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-; 

are less sensitive to chemical attack than polymers containing reactive silicon-hydrogen bonds. The lower homologs of poly(dimethylsilane),  $n = 2$  to  $7$ , are stable to cold concentrated sulfuric acid (128); a higher homolog,  $n = 55$ , is stable to aqueous bases (129). Insoluble poly(diphenylsilanes) exhibit resistance to attack by boiling aqueous alkali but undergo atmospheric oxidation in toluene solution at  $100^\circ\text{C}$  (130,131). Moist pyridine readily cleaves the silicon-silicon bonds of the Class 1 polymers with the formation of silicon-oxygen bonds. For use as dental materials, the properties of the Class 1 silicon polymers are not sufficiently outstanding to warrant further investigation; these polymers offer no advantages over the analogous carbon compounds.

The most industrially useful silicon polymers are the Class 2 polymers containing silicon-oxygen units in the polymer backbone. Several of the poly(organosiloxanes) exhibit physiological inertness and cause no foreign-body reaction by living tissue; both facts have suggested the use of poly(organosiloxanes) in medicine and medical research (118). The poly(organosiloxanes) may also prove valuable as adhesive restorative dental materials and as pretreatment coatings prior to application of a restorative dental material.

Appended organic groups on the silicon atoms were discussed in section ID as a means to vary the degree of polymer crosslinking. Silicone polymers that will probably be most useful as dental materials have the general formula represented below, where  $a$  is 1, 2, or 3:



Useful materials may also involve a mixture of various backbone units because of synergistic effects on the resulting polymer. The linear poly(siloxanes) have found their greatest usefulness as fluids or gums; the branched-chain poly(siloxanes) are useful as fluids or resinous solids of varying degrees of brittleness (125).

The silicon-oxygen bond is considered inert to hydrolysis; however, the hydrolytic stability of the poly(organosiloxanes) is better explained by the insolubility and poor wetting of the polymers than by the thermodynamic stability of the silicon-oxygen bond. Fox, Solomon, and Zisman (132) concluded that monolayers of poly(organosiloxanes) were subject to degradation by water, especially in the presence of dilute or concentrated acid or base. Although many bulk poly(organosiloxanes) are reported to be decomposed by acids and bases, the conditions of chemical attack are relatively drastic compared to the tooth environment. It is important to remember that the major uses of the poly(organosiloxanes) are under conditions of high temperatures. Therefore, it is necessary to investigate the reported experimental conditions carefully. For example, Hyde and DeLong (133) collected benzene in a cooled trap when diphenyldichlorosilane was hydrolyzed by moist air at 170°C. Rochow et al. reported this simply as "phenyl groups split off of silicon by strong acid" (114).

Dilute acids, salt solutions, dilute hydrogen peroxide, ammonium hydroxide, weak organic acids, and fatty acids have little effect on bulk poly(organosiloxanes) (123); however, Andrianov (116) reported that ammonium fluoride in the presence of sulfuric acid reacted under "mild" conditions with hexamethyldisiloxane to form trimethylfluorosilane. Alcohols do not chemically attack poly(organosiloxanes), but many organic liquids cause swelling or solution of some silicon polymers. An increase in the solvent and oil resistance of the poly(organosiloxanes) has been achieved by use of perfluoroalkyl (134,135) or cyanoalkyl (136,137) groups appended to the silicon.

The general chemistries of the poly(organosiloxanes) and inorganic silicates become similar as the number of appended organic groups becomes fewer. As the ratio of organic groups to silicon atoms becomes very small, i.e., the number of silicon-oxygen-silicon bridges becomes greater, the polymers change from liquids to rigid solids. The poly(organosiloxanes) that may be useful as dental materials will have to sacrifice some flexibility and ease of manipulation for the necessary rigidity of a dental material.

For dental materials use, the thermal stability of the poly(organosiloxanes) is of little concern, but several interesting points are noted. Lewis (138,139) confirmed that the presence of ionic impurities decreased the stability of the Si-O bond at high temperatures. The poly(phenylsiloxanes) are more stable to oxidative degradation than the poly(methylsiloxanes), and a synergistic effect is often observed when both methyl and

phenyl groups are present in the same molecule. As the number of carbons in the appended organic group is increased, the silicon-carbon bond becomes more susceptible to oxidative degradation at high temperature. Under severe hydrolytic conditions with strong acids, cleavage of the organic groups can occur. Phenyl groups are more susceptible to hydrolytic attack than alkyl groups under comparable reaction conditions.

The poly(ethylsiloxanes) are softer and more flexible than the poly(methylsiloxanes), while the poly(phenylsiloxanes) are brittle, resinlike substances with melting points that continue to rise on further condensation. An increase in physical strength and toughness of a poly(organosiloxane) may be achieved by the presence of both alkyl and aryl groups in the polymer. To provide special properties, many mixed poly(alkylarylsiloxanes) have been prepared with various substituents on the alkyl and aryl groups. Considering the number of usable organic groups and the number of variations within each group through the use of substituents, it is seen that an almost infinite variety of siloxane polymers is possible.

Since poly(siloxanes) are prepared by methods that could be adapted to dental applications, the general procedures used will be discussed briefly. The poly(organosiloxanes) are easily prepared through the intermediate formation of silanols  $\text{RSi(OH)}_3$ ,  $\text{R}_2\text{Si(OH)}_2$ , and  $\text{R}_3\text{Si(OH)}$ . The intermediate silanols are not isolated but rapidly undergo thermal or acid- or base-catalyzed polycondensation to poly(organosiloxane) and water (Fig. 5). The intermediate silanols are most commonly prepared in situ by the hydrolysis of chlorosilanes (A); also useful is the hydrolysis of alkoxysilanes (B), acetoxysilanes (C) and silazanes (D).

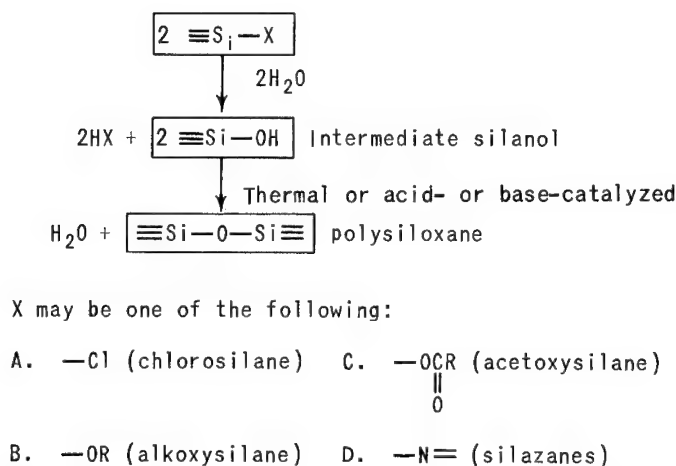
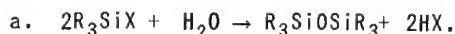


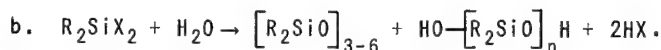
Fig. 5 - Method of preparation of poly(organosiloxanes)

The hydrolysis of monofunctional silanes yields disiloxanes

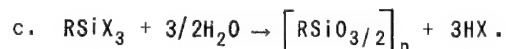


The hydrolysis of difunctional silanes yields the corresponding silanediol which undergoes polycondensation to a complex mixture consisting of both linear and cyclic poly(organosiloxanes) in a wide distribution of molecular weights:





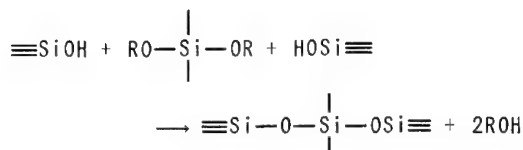
Trifunctional silanes undergo rapid hydrolysis to yield unstable silanetriols which undergo rapid intermolecular condensation to yield highly crosslinked resinous or crystalline materials:



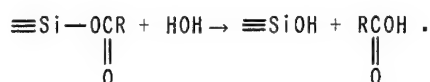
Silicone fluids are usually linear poly(organosiloxanes) prepared by equilibrating mixtures of cyclic poly(organosiloxanes) and disiloxanes or other sources of monofunctional groups. The acid- or base-catalyzed equilibrium reaction can be used to formulate industrially useful fluids of any desired viscosity. The resulting high-molecular-weight polymers remain in equilibrium with low-molecular-weight cyclic and linear poly(organosiloxanes). If the polymerization catalyst is left in the polymer, the high polymer degrades when it is heated under conditions in which the low-molecular-weight fraction is removed (cyclic tetramer boils at 160 to 170°C). The removal of ionic catalysts is essential and is done by batchwise procedures of washing, neutralizing or deactivating, and filtering. The use of quaternary ammonium and quaternary phosphonium bases as "transient" catalysts makes it possible to continuously polymerize the compounds; and when the catalyst is no longer needed, it is deactivated at a higher temperature than used during the polymerization. Tetramethylammonium hydroxide and tetra-n-butylphosphonium silanates were efficient "transient" catalysts (140). A possible use of the silicone fluids in dental applications is that of a tooth pretreatment medium similar to the use of siloxanes and silanes applied to glass surfaces. For example, vinyl silane glass-cloth sizes are used to present vinyl groups for reaction at the glass/air interface; the silane acts as a linking agent from the glass to organic resins (125).

Silicone rubbers consist of a mixture of long-chain siloxane gums, an inorganic filler, and an oxidizing agent. The filler is introduced to obtain the required reinforcement and affects the tensile strength, tear strength, and hardness; finely divided silica is the most used filler. The oxidizing agent, usually a peroxide, is used to induce crosslinking of the poly(organosiloxane) when the uncured rubber is heated to 150 to 250°C. Although silicone rubbers may not be applicable as dental materials, several points that may be important to resinous silicones will be considered. By the proper control of the polymer-filler interaction, fillers or reinforcing materials have been successfully used to produce high-tensile-strength silicone rubbers. A study of reinforced silicon resins may be fruitful in formulating useful dental materials. The silicone polymer-filler interactions that cause "crepe-aging" or "structure" formation may be a disadvantage, since the reaction reduces the shelf-life of the materials; however, additives have now been formulated to control this phenomenon. Various additives to the silicone rubbers have also been used to increase thermal stability, reduce compression set, and add color.

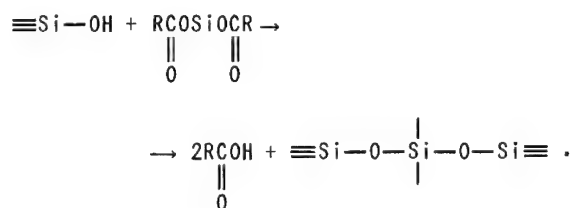
To produce optimum physical properties, a final thermal curing of silicone rubbers is an essential part of the application technique; therefore, most silicone rubbers cannot be used with heat-sensitive materials, or in locations where temperatures between 150 and 250°C are not permissible. The recent introduction of room-temperature vulcanization (RTV) has made it possible for some materials to circumvent the thermal restrictions. This has been accomplished by use of various groups to affect the crosslinking of vulcanization; additives used include alkoxysilanes with metallic salts of carboxylic acids (141-145), acetoxysilanes (146,147), and other polyfunctional compounds, for example, boric acid (148). The probable crosslinking sequence is



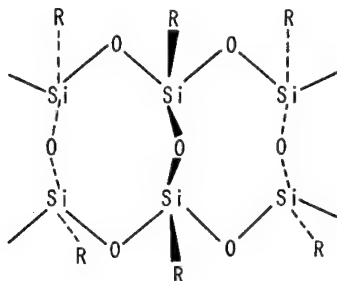
for an alkoxy reaction in which an alcohol is the byproduct. Hydrolysis of the acetoxy-silicon groups by atmospheric moisture can be effective in curing the silicone rubbers by forming the corresponding silanol and carboxylic acid:



The resulting hydroxyl groups may crosslink, or the acetoxy-silane compounds can react directly with the silanol



The silicone resins are characterized by the presence of ring structures and by a much higher degree of crosslinking than is found in the siloxane elastomers. The ratio of organic groups to silicon atoms in silicone resins is generally between 1.0 and 1.6; brittle, infusible, insoluble materials are produced when the ratio approaches 1.0 for maximum random crosslinking. Controlled condensations have been used to prepare stereoregular double-chain structures:

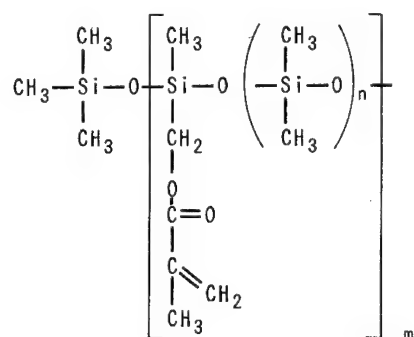


For example, alkyl- or arylsilsesquioxanes form syndiotactic chains joined in turn through cis-fusion at each unit to give a ladderlike linear network (149-152). The phenylsilsesquioxane or "phenyl-T" is soluble in benzene, tetrahydrofuran, and methylene chloride; the high-molecular-weight material is stable to 400°C with no melting.

Since most uncured silicone resins are tacky solids, they are usually handled in suitable solvents; examples are silicone paints and electrical varnishes. After solvent evaporation, the thin resin films are baked to effect a proper "cure" by further crosslinking; this procedure would not be possible for dental materials. A solventless resin

system has been reported that consists of a vinyl siloxane and a liquid siloxane containing at least two silicon-hydrogen groups per molecule (153). The preformed resin is produced by heating the mixture between 50 and 110°C in the presence of a platinum catalyst; the final cure is from 110 to 200°C. A combination of poly(organohydrogensiloxanes) and a RTV catalyst, for example tetraethoxysilane, has been reported to produce materials that cure rapidly in the presence of water (145). The products have been suggested for use as prosthetics, dental molding compounds, and fillings for tooth roots.

The properties of silicone resins depend on the ratio of organic groups to silicon, the nature of the organic group, and the preparative method of hydrolysis and curing (123). Some silicone resins, especially those rich in phenyl groups, are compatible with organic resins; the two types of resins may simply be mixed together for many uses. Copolymers may be prepared by reaction of residual silanol groups or alkoxy-silicon groups in a poly(organosiloxane) with suitable functional groups in organic polymers; the properties of the modified resins depend on the nature of the polysiloxane, the organic polymer, the order of reaction, and the degree of condensation. Bulatov, Spasskii, and Mishina (154) used a functional acetoxy group, methacrylate, on the poly(organosiloxane)



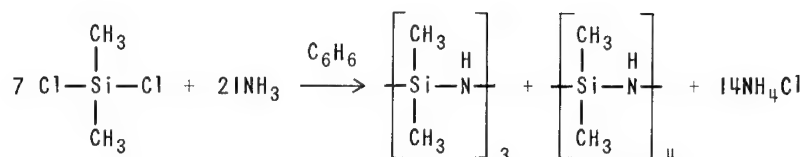
to copolymerize with unsaturated organic compounds, for example, styrene monomers. The products were crosslinked insoluble glasses.

The number of silanol groups remaining in uncured resins will determine the shelf-life of the resin; condensation and crosslinking reactions continue at a rate determined by the temperature, the resin concentration, and the nature and number of substituent groups on the silicon. The continuous condensation is minimized in the dry, solventless resins. Although some disadvantages have been mentioned, the use of poly(organosiloxanes) for dental materials is most probable. Resins containing fillers and reinforcement fibers cured by techniques similar to the room-temperature vulcanizing method should be investigated.

Although random cyclic units may be present in some resinous materials and in some fluids (155), attempts to utilize the cyclic siloxanes by systematically linking them together, as in boron and phosphorus cyclic systems, has not been reported.

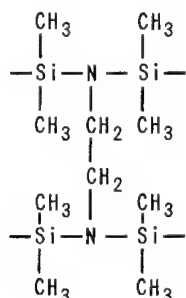
The Class 2 polymers containing silicon-nitrogen repeating units, the poly(organo-silazanes), generally suffer from extreme hydrolytic instability; consequently, the poly(organo-silazanes) are a source of silanol intermediates in the preparation of poly(organo-siloxanes) (156-159) and may find use in dental applications. The polymer system will be briefly discussed because of its potential usefulness.

Linear polymer formation is difficult because of the ease by which cyclic trimeric and tetrameric organosilazanes form when a dichlorosilane is treated with ammonia:

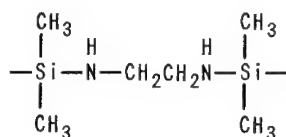


The hydrolytic instability and ease of ring formation are attributed to the ability of nitrogen to donate electrons. Any interaction of the extra nitrogen electron pair with the d orbitals of silicon will decrease the donor properties of nitrogen in proportion to the degree of electron involvement; the change to a higher silicon-nitrogen bond order, through coordination, should cause a significant change in polymer properties.

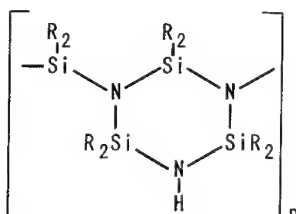
Minné and Rochow (160,161) studied the effect on hydrolysis of coordinated metal ions with polymeric organosilylamines. The tetrahedral-coordinated beryllium significantly reduced the rate of hydrolysis compared to the uncoordinated polymer. Square-planar coordinated copper led to a polymer rearrangement and produced a copper-free ladder polymer:



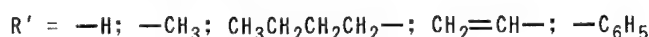
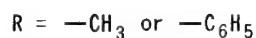
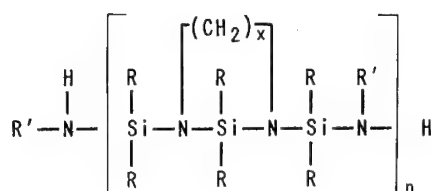
The resulting polymers were only slowly hydrolyzed by water, but in the presence of acid the reaction rate was greatly increased. The diamine linkage between the silicon atoms was used to prevent cyclization of the polymer and to increase the silicon-nitrogen stability by using carbon links between units:



Krüger and Rochow (162) prepared colorless waxes that were reported to contain trimeric organosilazane rings linked together by a dialkyl- or diarylsilane group:



An approach to stabilizing the linear silicon-nitrogen polymers against cyclization is the use of a bridged group between the 2 and 4 positions of the repeating silicon-nitrogen unit:



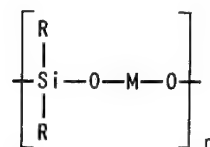
To summarize, the further evaluation of the silicon-nitrogen polymer systems for dental materials is inadvisable because of their hydrolytic instability; however, the poly(organosilazanes) may be useful as pretreatment coatings for dental applications because the polymers are easily hydrolyzed to poly(organosiloxanes). It is of interest to note the reverse hydrolytic-stability order of the silicon-oxygen-silicon and silicon-nitrogen-silicon bonds as compared to the same linking atoms with boron and phosphorus; the boron-nitrogen-boron and phosphorus-nitrogen-phosphorus bonds are hydrolytically more stable than the corresponding boron-oxygen-boron and phosphorus-oxygen-phosphorus bonds.

The incorporation of metal atoms into poly(organosiloxane) structures to enhance thermal stability has been the major stimulus to the study of poly(elementosiloxanes), Class 3 silicon polymers having silicon-oxygen-element repeating units (Table 3). Professor K.A. Andrianov in Russia (166-170) and Professor D.C. Bradley in Canada and England (171-173) have been major contributors to the knowledge of the poly(elementosiloxanes). The poly(elementosiloxanes) generally have thermal and hydrolytic stabilities inferior to the parent poly(organosiloxane) and do not appear to offer any advantages over the poly(organosiloxanes). Since the effects that are caused by the inclusion of foreign atoms in the poly(siloxane) structure are important for the formulation of dental materials based on Class 2 silicon-oxygen polymer systems, the poly(elementosiloxanes) will be briefly discussed with emphasis on polymer properties. More detailed information may be found in the references cited; Jones (126) has published a two-part review of the poly(elementosiloxanes).

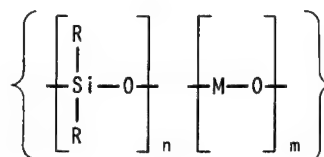
Table 3  
Elements Which Will  
Form Poly(elementosiloxanes)  
Containing  $\text{—Si—O—M—}$   
Repeating Units

Group	Element (M)
III	B Al
IV	Ge Sn(II) Sn(IV) Pb
V	P As(III) As(IV) Sb
VI	S(VI)
Transition metals	Ti(IV) V Cr(VI) Fe(III) Co Ni Zr(IV)
Other metals	Mg Cu(II) Zn Hg(II)

The inclusion of a foreign element into the poly(organosiloxane) structure may be in a regular fashion



or in a random fashion as isolated linkages throughout the polymer structure



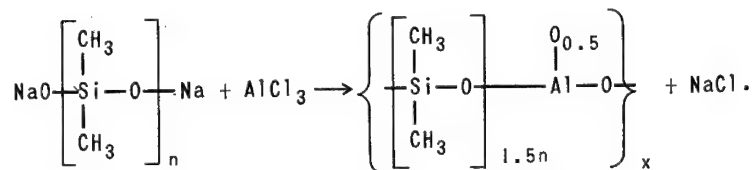
In either case, the foreign element causes an increase in the polar or ionic character of the resulting polymer. If the foreign element has an electronegativity greater than silicon, the greater  $p_\pi\text{—}d_\pi$  interaction between the foreign element and oxygen than between silicon and oxygen will create points along the polymer backbone of higher polarity than the silicon-oxygen bonds. The thermal stability of the poly(metallosiloxanes) would be expected to increase compared to the parent poly(organosiloxane); however, the increased ionic character would also cause a loss of flexibility and a possible decrease in the polymer stability toward water, acids, and bases. A systematic study of the hydrolytic stability of

poly(metallosiloxanes) has not been reported yet. The reaction of hydrochloric acid at 90°C with poly(aluminoxane-phenylsiloxane) and poly(titanoxane-phenylsiloxane) has been compared (169,174). The investigation revealed that the silicon-oxygen-titanium linkage was hydrolytically more stable than the silicon-oxygen-aluminum linkage, but not as stable as the silicon-oxygen-silicon linkage. The increased ionic nature of the foreign atom-oxygen bond provides increased probability of nucleophilic attack on the poly(organosiloxane) backbone.

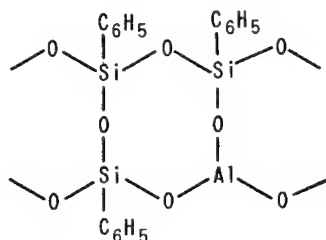
The most widely known poly(borosiloxane) is "bouncing putty," poly(borodimethylsiloxane), in which there is one boron atom to every 3 to 100 silicon atoms in the backbone. Other than as a plaything for children, bouncing putty has found little application, primarily because of its susceptibility to hydrolysis; the silicon-oxygen-boron linkages are hydrolyzed to form boric acid and a low-molecular-weight poly(organosiloxane). Hydrolytically stable poly(borosiloxanes), which are structurally related to bouncing putty, have been reported by Wick (175). The elastomers contain less than one boron atom to 100 silicon atoms and have molecular weights over 70,000 and usually between 350,000 and 500,000. A nonviscous, elastic material is obtained when the polymer is vulcanized. An interesting property of the vulcanized material is its ability to self-weld; however, on prolonged contact with atmospheric moisture, the material is rendered

incapable of self-welding at room temperature and self-welds only feebly at temperatures above 100°C. The self-welding property of the poly(borosiloxane) may be useful as a pre-treatment coating before using a dental restorative material. If the boron content is increased beyond the designated limit even by the most insignificant amount, a new product resembling bouncing putty is obtained. The sharp change in properties indicates that the ratio of silicon to foreign element is very important for determination of the resulting poly(elementosiloxane) properties; deteriorative effects may be found at one ratio and beneficial effects at another ratio.

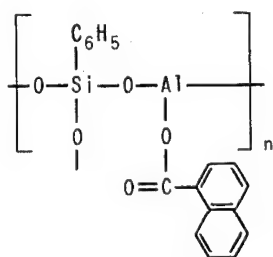
Poly(aluminosiloxanes) have been reported with randomly dispersed aluminum and regularly dispersed aluminum in the polymer backbone. The methods of preparation for both types of polymers are also typical procedures used to prepare other poly(metallosiloxanes). A range of poly(aluminodimethylsiloxanes) with silicon-to-aluminum ratios from 0.8 to 23.3 were prepared by the reaction of aluminum chloride with the sodium salt of poly(dimethylsiloxane) (176):



The polymers that had low silicon-to-aluminum ratios, 0.8 and 1.3, were brittle, insoluble solids, indicative of a three-dimensional structure. Polymers having high silicon-to-aluminum ratios, 6.8 and 23.3, were soluble in both polar and nonpolar solvents even after heating for 6 hours at 150°C. An outstanding characteristic of poly(aluminophenylsiloxane), having a silicon-to-aluminum ratio of 4, is the complete infusibility but ready solubility in organic solvents; the polymer can be plasticized. A "cyclolinear" or ladder-like double-chain structure similar to phenylsilsesquioxane has been proposed for the poly(aluminophenylsiloxane) structure (177):



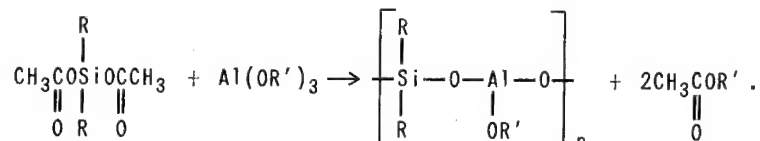
Aluminum naphthenate and disodium phenylsilanate have been used to prepare poly(naphthenoaluminophenylsiloxanes) that are soluble in most organic solvents but insoluble in alcohols (178):



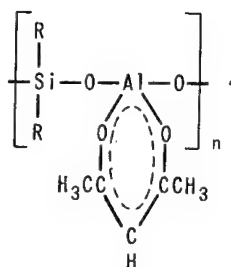


The low mechanical strength of the polymer was increased 200 percent by heating the material for 10 hours at 120°C.

Poly(metallosiloxanes) containing aluminum in a regular repeating unit are generally prepared by the polycondensation of dialkyldiacetoxysilane and a metal alkoxide, for example, dimethyldiacetoxysilane and aluminum alkoxide:

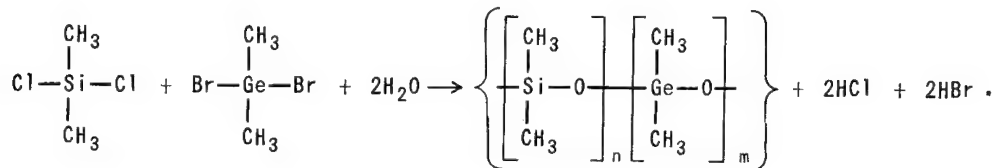


The preparative method has also been successful with metals having attached chelating groups for increased hydrolytic stability (179,180). For example, diisopropoxyaluminum acetylacetonate has been used to prepare poly(aluminosiloxanes) of the type



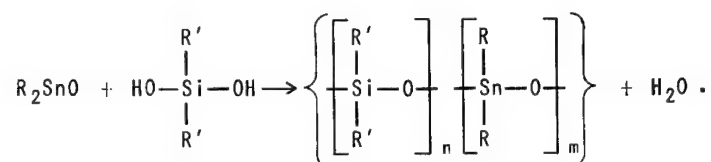
Soft resins, waxes, and powders were isolated after melting the products or heating under reduced pressures. The properties were changed within 4 to 6 hours on contact with moist air (179).

Another method of forming poly(metallosiloxanes) with varying silicon-to-metal ratios is illustrated by the aqueous-alcohol cohydrolysis of dimethyldichlorosilane and dimethyldibromogermane:

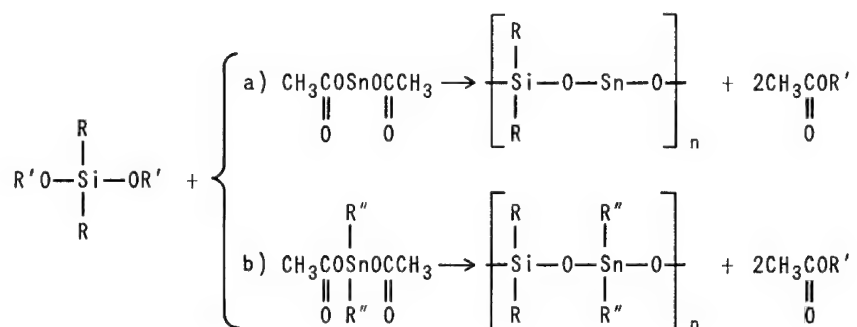


The low-molecular-weight poly(germanosiloxane) is further polymerized by concentrated sulfuric acid to give a soft rubberlike material (181). The thermal stability of the poly(dimethylgermanodimethylsiloxane), silicon-to-germanium ratio 19, showed no substantial change from the corresponding poly(dimethylsiloxane). The random inclusion of tin atoms in a poly(siloxane) backbone has also been achieved by the cohydrolysis of dihalosilanes and dihalostannanes (182). The final composition of polymers obtained by cohydrolysis is dependent on the rates of hydrolysis of the silicon and metal halides and on the ease with which self-condensation or intercondensation occurs with the intermediates of hydrolysis.

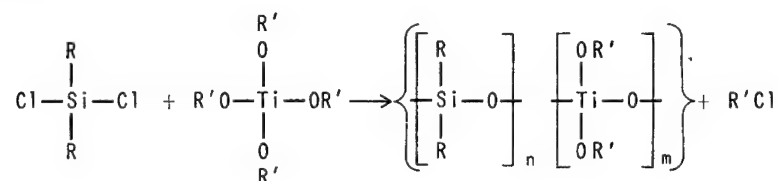
The reaction of dialkyltin oxide with a dialkyl- or diarylsilanediol has also been used to prepare poly(stannosiloxanes) with varying silicon-to-tin ratios:



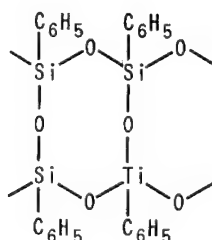
Crain and Koenig (183) studied the hydrolytic stability of a poly(stannosiloxanes) series having varying silicon-to-tin ratios; the 24-hour tests were conducted in room-temperature water. Poly(dimethylstannodiphenylsiloxane) was found to be most stable when the silicon-to-tin ratio was large, that is, when the amount of tin in the poly(siloxane) backbone was small. Regular inclusion of tin in the polymer chain is achieved by reacting dialkyl-dialkoxysilane with diacetoxystannane [Sn(II)] or dialkyldiacetoxystannane [Sn(IV)] (184):



Poly(titanosiloxanes) can be prepared by the cohydrolysis of dichlorosilanes and titanium alkoxides



or by any of the poly(elementosiloxane) preparative methods already discussed (185). The regular inclusion of titanium in the polymer chain is obtained by the reaction of titanium alkoxides with diacetoxysilanes. A poly(titanophenylsiloxane) with a silicon-to-titanium ratio of 3



was reported to be a brittle, glasslike material (168). The polymer is relatively stable toward the action of hot hydrochloric acid solutions (169,174); 1.5% of the titanium is solubilized in 10% hydrochloric acid, 15% in 20% acid, and 50% in 30% acid. As mentioned earlier, the silicon-oxygen-titanium bond has a higher hydrolytic stability than the silicon-oxygen-aluminum bond in comparable poly(metallophenylsiloxanes).

Poly(phosphosiloxanes), poly(arsenosiloxanes), and poly(stibinosiloxanes) are readily susceptible to hydrolysis and attack by acids and bases (166). A qualitative study of poly(metallosiloxanes), some only short-lived intermediates, has been reported by Hornbaker and Conrad (186); the polymers contained tin(II), lead(II), magnesium, copper(II), zinc, and mercury(II) ions in a poly(siloxane) chain. The materials isolated were easily decomposed to poly(siloxanes) and the corresponding metal oxide. Further study of these unstable materials may lead to a means of preparing metal-oxide-reinforced poly(siloxanes) useful for dental materials. Poly(siloxane) chains containing both iron and aluminum have also been reported (187).

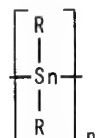
To summarize, the poly(organosiloxanes) appear to be a class of inorganic polymers which should be evaluated for possible use as dental materials. Since the interest in poly(organosiloxanes) and poly(elementosiloxanes) has been directed toward finding thermally stable materials, none of the polymers have been critically evaluated for reactivity toward water, acids, and bases. The increased ionic character of the poly(metallosiloxanes) is not favorable for hydrolytic stability; these polymers may not be suitable for dental restorative material but may find use as pretreatment coatings or as reactants in the formation of reinforced plastics.

## 2. Germanium, Tin, and Lead Polymers

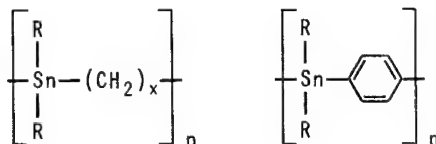
The germanium polymers that have been reported are rather low-molecular-weight substances susceptible to attack by acids and bases (188,189). In general, the polymeric germanium compounds decompose to lower-molecular-weight materials in a reversible way; for example,  $[(C_6H_5)_2GeO]_4$  forms a high polymer,  $[(C_6H_5)_2GeO]_n$ , in a water-ethanol solution and reverts to the tetramer when treated with acetic acid (190). A similar depolymerization is noted for the polymer  $[(CH_3)_2GeO]_n$  (191). Because of the moisture present in the tooth environment and the fact that no by-products are involved in the polymerization, the formation of the germanium polymers in the presence of water is of interest. The germanium polymers, however, offer no advantage over the Class 2 or Class 3 silicon polymers; and the Class 1 polymers (192) offer no advantages over the analogous carbon compounds. Further consideration of the germanium system as dental materials is not deemed advisable.

The physiological properties of tin are unique; inorganic compounds of tin are generally accepted as being nontoxic, while organotin compounds are generally highly toxic (193). Several organotin compounds have found use as agricultural fungicides and as the active ingredient in antifouling paints. Tin polymers suggested for use as dental materials would require careful evaluation of their physiological properties. Gilman et al. (193) and Neumann (194) have reviewed the recent developments in organotin chemistry; discussions of polymers containing tin are included.

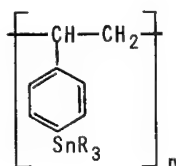
Class 1 polymers, for example, dialkylstannanes



are readily oxidized and are sometimes spontaneously flammable (195,196). The Class 3 tin polymers containing silicon-oxygen-tin units have been discussed in the silicon section (197). Only the Class 2 tin-oxygen and tin-carbon polymers exhibit properties which appear to be compatible with dental material properties; however, the tin polymers offer no apparent advantages over the analogous silicon polymers. Tin-carbon linkages have been reported in the polymer backbone

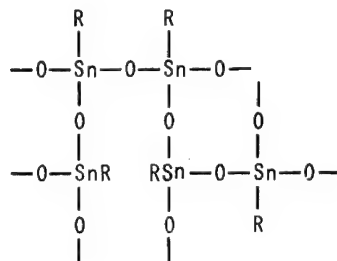


(197-200) or in a side group of an organic polymer (201):

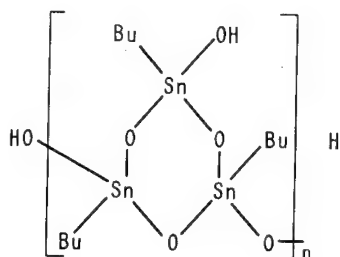


The properties of the tin-carbon polymers are not expected to be compatible with dental material requirements.

Class 2 tin-oxygen polymers have been reported to exhibit several interesting properties. Polymers derived from alkane stannonic acids,  $\text{RSn}(\text{O})\text{OH}$ , are reported to be hydrolytically stable, insoluble in most organic solvents, and soluble in lower aliphatic alcohols through the probable formation of organotin esters; evaporation of excess alcohol and heat treatment of the residue produces products that are transparent plastics (Noltes, 198):

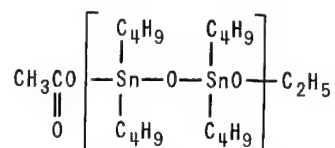


Zhivukhin, Dudikova, and Pshiyalkovskaya (202) reported the preparation of a white infusible material by thermal dehydration of 1-butanestannonic acid. The product was boiled in water for 8 hours without loss in weight or change in elementary composition; no mention of acid or base attack was made, but reaction with these reagents is predicted. The proposed structure of the polymer

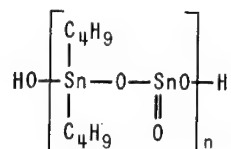


differs from that given by Noltes (above).

Poly(stannoxanes), examples of which are given in Table 4, are generally stable toward hydrolysis and alkali attack but react with halogen acids to form the corresponding organotin halide. The low-molecular-weight materials have found use as polyvinyl chloride stabilizers. Koton and Kiseleva (209) isolated a benzene-soluble tetrameric dibutylstannoxane

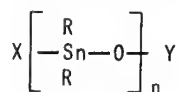


which hydrolyzed to an insoluble and infusible material:



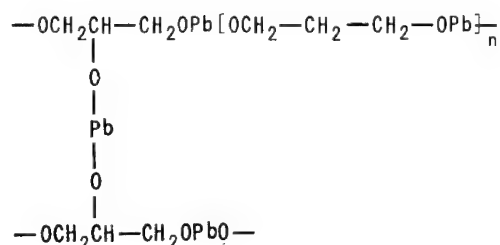
Polymerization by hydrolysis would be a desirable property for dental materials. A thorough investigation of the relationship between appended organic groups on tin atoms and acid attack at tin-oxygen bonds in poly(stannoxanes) is needed.

Table 4  
Poly(stannoxanes)



X	Y	R	n	Reference
R'O—	—R'	Alkyl or Aryl	2 to 5	203-205
$\begin{array}{c} \text{O} \\    \\ \text{R—C—O—} \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{—CR}' \end{array}$	Alkyl	1	206
C <sub>4</sub> H <sub>9</sub> —	—Sn(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	—C <sub>4</sub> H <sub>9</sub>	2, 5, and 14	207
HO—	—H	—CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	8 or 9	208

Unlike tin, both inorganic lead compounds and organolead compounds are toxic, although the latter compounds exhibit the greatest toxicity. A familiar lead polymer is the glycerin-litharge cement which forms a hard, insoluble, and infusible product; the structure of the resulting lead glycerates probably consists of a mixture of chains and crosslinkings:



The possible toxicity, the low molecular weight of the polymers, and the ease of chemical attack on the polymers were factors which influenced our decision to exclude the lead polymers from further consideration as possible dental materials.

### C. Group V: Phosphorus, Arsenic, and Antimony

#### 1. Phosphorus Polymers

The extreme toxicity of some esters and amides of phosphorus acids is well known by their application as chemical-warfare agents and insecticides (210); therefore, any phosphorus-containing polymers which may have suitable dental-material properties should be carefully evaluated for toxicity in environments similar to the mouth. Since there is seldom mention of the physiological properties in the vast literature pertaining to the three classes of phosphorus polymers, the potential toxicity of the phosphorus polymers must be kept in mind.

Class 1 phosphorus polymers, the phosphines, are not suitable as dental materials because of low molecular weights and chemical instability of catenated phosphorus atoms. The large volume of literature pertaining to Class 2 phosphorus polymers attests to the industrial hope of some day synthesizing useful inorganic phosphorus polymers. Several systems of the Class 2 phosphorus polymers have characteristics which are consistent with properties desirable for dental materials. The following discussion will be concerned mainly with the Class 2 polymers containing phosphorus-oxygen and phosphorus-nitrogen polymer-backbone units. Based on our definition of inorganic polymers, polymers with phosphorus-carbon units will not be discussed. Some polymers of phosphorus esters, Class 3 polymers containing phosphorus-oxygen-carbon backbones, have already been investigated as potential dental materials which do not have the inherent weaknesses exhibited by organic polymers tested as restorative dental materials (211). Although carbon is a constituent of the phosphorus ester polymer backbone, it is important to consider, as was done in the boron section, the stabilizing effect organic groups have on hydrolytically unstable linkages. To this extent, organic moieties in the polymer backbone will be included.

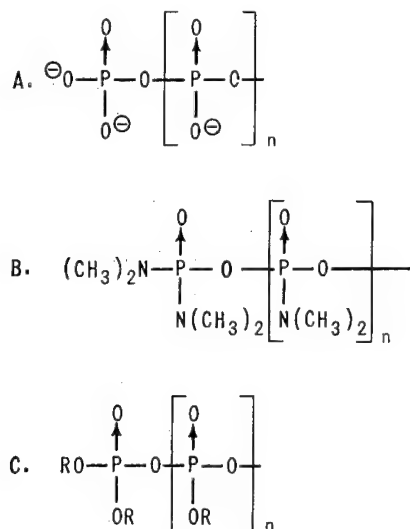
The mineral portion of teeth consists of hydroxyapatite, the only solid phase of the calcium phosphate-water system which is stable at neutral pH. Also present are such ions as sodium, magnesium, potassium, chloride, fluoride, carbonate, and citrate; other materials in trace amounts have been found also. The presence of phosphorus-oxygen systems in the highly complex tooth structure suggests the Class 2 phosphorus-oxygen polymers as candidates for dental materials.

Dry poly(phosphates) are hard, brittle materials which can be plasticized by water, but they are hydrolytically unstable and pH sensitive. Since poly(phosphates) are precipitated by proteins in acid media, various cations, organic quaternary ammonium ions, pyridinium ions, and chelates of multiply charged cations have been studied in an unsuccessful attempt to stabilize the poly(phosphate) structure against hydrolytic attack (212-215).

Poly(phosphates) (chain structures) and metaphosphates (ring structures) have been reported which are stable toward hydrolysis. Two materials, Kurrol's salt and Maddrell's salt, consist of phosphorus-oxygen chains of interconnecting  $\text{PO}_4$  tetrahedrons of molecular weights from 250,000 to several million (214,215). Both salts are negligibly soluble in water at room temperature, but Kurrol's salt is readily soluble in solutions containing other alkali metal ions.

Because of the charge interaction, pure metal salts of the long-chain poly(phosphates) are rigid glasses in the amorphous state. Interesting properties of the soluble poly(phosphates) are the ease with which they can be plasticized with small amounts of water and the increased flexibility obtained by using unusual cations. For example, quaternary ammonium ions with at least one bulky organic radical contribute sufficient charge separation for flexibility (212,213,216,217). The hydrolytic instability of these materials precludes their use as dental materials; however, Maddrell's salt,  $\text{NaPO}_3$ , which is known as insoluble metaphosphate or "IMP," is used as a dentifrice polishing agent because of its mild abrasive action.

The poly(phosphate) chain (A) has been altered by appending amide (B) (218) and ester (C) (219) groups to the phosphorus atoms in the polymer backbone:



The resulting materials are susceptible to hydrolysis in varying degrees, but compositions containing no branch points do not react immediately with water at room temperature or below. Evidently the branch chains promote a point of weakness for hydrolytic attack. The kinetics of condensed phosphate hydrolysis has been summarized by Gimblett (220), Thilo (214,215), and Van Wazer (212).

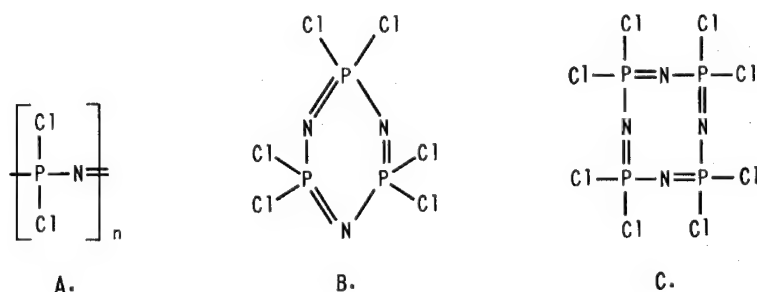
Another distinct disadvantage of the Class 2 phosphorus-oxygen polymers is the formation of most poly(phosphates) by thermal polycondensations. Not only should future poly(phosphate) research be directed toward chemical stability, but new methods of preparation must be investigated. An understanding of the formation and degradation of

poly(electrolytes), for example, poly(phosphates), poly(tungstates), poly(molybdates), and poly(chromates) in aqueous solution may provide new means of preparing polymers applicable as dental restorative materials. A new and radical approach to filling a tooth cavity may result from investigations of insoluble poly(electrolyte) formation within the tooth cavity from aqueous solutions at the proper pH; present packing methods should not be a restriction for the dental materials desired. The field of poly(electrolytes) has been reviewed by Tobias (221) and Sillén (222).

Class 2 phosphorus polymers which have been most studied over the longest period are those compounds containing phosphorus-nitrogen linkages in a repeating unit. The most publicized system which has challenged any researcher who has ever thought about inorganic polymers is the phosphonitrilic polymers, sometimes referred to as phosphonitriles or phosphazenes. The literature pertaining to these compounds is voluminous, and the recent review articles (223-229) should be consulted for more detailed discussions. The first comprehensive review of the literature pertaining to the phosphonitrilic compounds was by Audrieth, Steinman, and Toy (230) and is an excellent review of the early literature.

Although an extensive effort has been devoted to the study of the phosphonitrilic halides and their derivatives, none of the materials prepared so far has presented a challenge to organic polymers. Although no useful phosphonitrilic polymers have been produced for large-scale use, the possibility of finding phosphonitrilic polymers for relatively small-scale specialty uses—for example, as an adhesive restorative dental material—seems plausible. Most phosphonitrilic polymers that show possible use as dental materials may be eliminated from final consideration because of the preparative method; therefore, the important problems encountered in preparation will be emphasized more in this section than in the others.

The compounds that originally attracted attention to the polymeric phosphonitriles were the chlorides,  $(Cl_2PN)_n$ , which formed an unstable rubber (A) when the cyclic trimer (B) or tetramer (C) was heated between 250 and 350°C:



Unfortunately, the "inorganic rubber" degrades under normal atmospheric conditions much more rapidly than organic rubbers. Extensive study of the formation and polymerization mechanisms of the cyclic phosphonitrilic chlorides has been reported, but they are not within the scope of this report; the several reviews and papers by Becke-Goehring (231-234) and Gimblett (235) should be consulted for further information.

Like the siloxanes and boron-nitrogen polymers, the low-molecular-weight cyclic phosphorus-nitrogen compounds are thermodynamically more stable and more resistant to hydrolytic attack than the linear materials. Although phosphonitrilic chloride trimer can be steam distilled, higher-molecular-weight cyclic and linear homologs are decomposed under the same conditions. In general, the polymeric phosphonitrilic halides and mixed halides are susceptible to hydrolysis; the formation of hydrolytically stable derivatives has been a major effort of researchers in the phosphonitrilic field. Organic groups



appended to the ring phosphorus have been varied extensively in attempts to stabilize the cyclic and linear phosphonitrilic polymers. However, only a few of the phosphonitrilic organic derivatives have received systematic attention; and the literature merely records the existence, the preparative method, and possible uses.

The methods of preparation of the phosphonitrilic derivatives are by (a) a substitution reaction of a group on the ring phosphorus, usually the cyclic trimer with a nucleophilic reagent or (b) use of the proper organophosphorus reagent in the initial preparation of the phosphonitrilic derivative. The phosphonitrilic derivatives are too numerous to be thoroughly considered in this report. Groups reported appended to phosphorus are listed in Table 5; relatively complete listings of derivatives and methods of preparation are given by Haber (225), Shaw (228), Hedger and Barb (236), and Turashev (237). The interesting stereochemical possibilities encountered when partially substituted cyclic trimeric and tetrameric derivatives are prepared will not be of consequence to the following discussion. (See Refs. 227-229, 238-242).

Table 5  
Derivatives of Cyclic and Linear Phosphonitrilic  
Compounds,  $[X_2PN]_n$

Group	X
Halide	F, Cl, Br, and mixed halides
Azide	$N_3$
Isothiocyanate	NCS
Hydrazide	$N_2H_3$
Phosphazeryl	$-N=P(C_6H_5)_3$
Amine	$NH_2$ , $NHR$ , $NR_2$
Ester	$-OR$ ( $R = CH_3$ , $C_2H_5$ , $(CH_3)_2CH$ , $C_4H_9$ , $CH_2CF_3$ , $CH_2C_2F_5$ , $CH_2C_3F_7$ )
Alkyl	$CH_3$ , $C_2H_5$ , $CF_3$ , $C_3F_7$
Aryl	$C_6H_5$

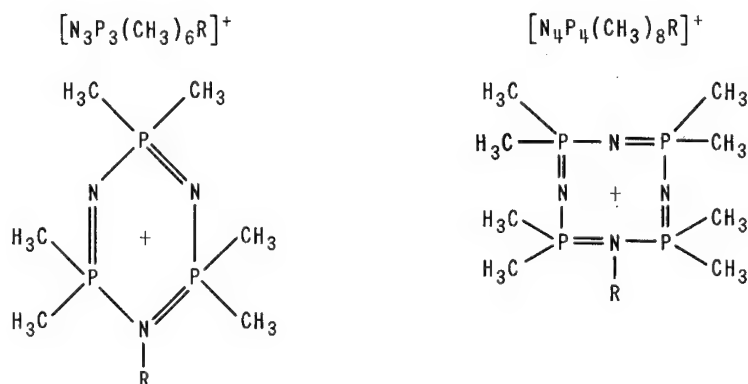
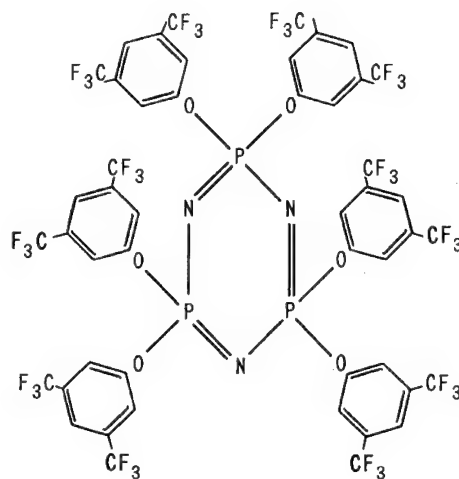
Studies of the thermal polymerization of cyclic phosphonitrilic chlorides indicated that a preliminary phosphorus-chlorine ionization is involved (243-246) and not a free radical mechanism (247-249). Oxygen initiates the thermal condensation and acts as a chain terminator and crosslinking agent; the polymerization to high-molecular-weight chain polymers does not occur if oxygen is excluded. The higher polymers formed during the thermal treatment, 200 to 300 °C, of cyclic trimeric and tetrameric phosphonitrilic chlorides range from oils to elastomers with some molecular weights in excess of 100,000 (228). However, the high-molecular-weight products are easily hydrolyzed, with the liberation of hydrochloric acid. High pressures and temperatures do not alter the nature of the products but do slow the rate of high-polymer formation (250).

All trimeric phosphonitrilic halides and mixed halides undergo thermal polymerization to high-molecular-weight chain polymers. Derivatives which contain only organic groups on the ring phosphorus do not polymerize under the thermal conditions noted, but rather undergo thermal decomposition at elevated temperatures. For example, under conditions

which cause high-polymer formation of trimeric phosphonitrilic halides, the pure phenoxy derivative,  $[(C_6H_5O)_2PN]_3$ , is completely unaffected by heat (251,252). Some cyclic derivatives, for example fluorophenoxy compounds, have exhibited possible usefulness as high-temperature oils because of their resistance to polymerization at elevated temperatures (251). The water-stable bis(3,5-trifluoromethyl)phenoxy phosphonitrilic trimer did not form solids or acid when heated at 200°C for 48 hours with water in a sealed tube.

Three methods for the elimination of reactive halogen from cyclic or linear phosphonitrilic polymers are: (a) nucleophilic substitution of the halogens on the phosphorus-nitrogen ring followed by ring cleavage and high-polymer formation; (b) formation of linear high polymers of phosphonitrilic halide followed by the nucleophilic substitution of the active halogens on the chain; (c) the preparation of linear polymers from starting materials which have the desired phosphorus substituents. The merits of each method of preparation will be briefly summarized in the following discussion.

The derivatives of trimeric and tetrameric phosphonitrilic halides which can be used as cyclic pseudo-monomers for high polymers are listed in Table 5. As previously stated, the polymerization of the organic derivatives of phosphonitrilic halides proceeds with difficulty when the usual thermal methods of polymerization are employed. The decomposition of the derivatives usually occurs at the elevated temperatures and other less desirable polymers may be formed. For example, the thermal decomposition of the ethoxy derivative,  $[(C_2H_5O)_2PN]_{3,4}$ , forms ethyl ether and polymers highly crosslinked through phosphorus-oxygen-phosphorus bonds (253). If the cyclic phosphonitrilic derivatives are to be useful as pseudo-monomers, other means of initiating ring rupture for linear polymer formation must be investigated. The study of the reported formation of water-soluble and water-stable N-alkylphosphonitrilium salts

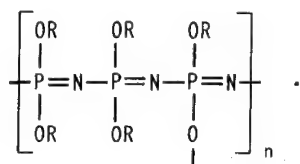


by the reaction of an alkyl iodide with the alkyl derivative of phosphonitrilic trimer or tetramer (254) may elucidate the mechanism of ring cleavage.

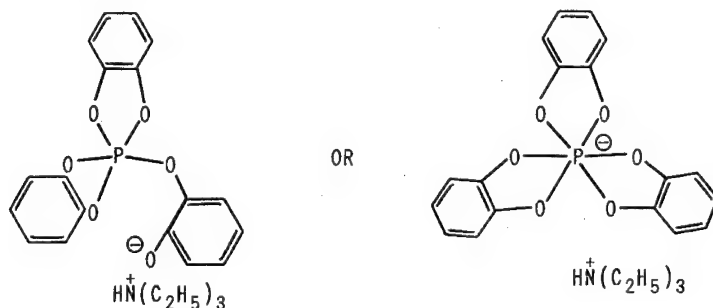
Lakatos et al. (255) reported no complex formation between cyclic phosphonitrilic chlorides and transition metals; however, water-sensitive metal chloride adducts of

linear phosphonitrilic polymers have been prepared by the inclusion of a Lewis acid, for example, during the reaction of phosphorus(V) chloride with ammonium chloride (251,256). The difference between the adducts of phosphonitrilic halides and the adducts of substituted derivatives needs to be investigated more completely.

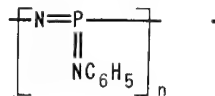
The formation of phosphonitrilic derivatives from preformed linear poly(phosphonitrilic) halides has the disadvantage of incomplete halogen removal. Treatment of linear poly(phosphonitrilic) chloride, "inorganic rubber," with an ethanol-pyridine mixture at room temperature produced a white, tacky, slightly elastic solid (257). A gray-white rubber, which was described as resistant to cold water, was obtained when a trifluoroethanol-pyridine mixture was used. The chloride replacement is high, 90 to 95%, but evidently not all are replaced. Some crosslinking through phosphorus-oxygen-phosphorus bonds was postulated for the structure of the products:



It is important to note that the reaction of a catechol-triethylamine mixture with polymeric phosphonitrilic chloride ( $\text{---Cl}_2\text{PN---}_n$ ,  $n \approx 1500$ ) resulted in a product which no longer contained phosphorus-nitrogen bonds after it was washed with water and with methanol (258, 259). The proposed structure of the final product is

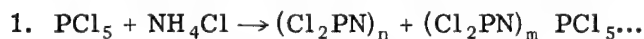


A variation of the above method has been used in which the phosphonitrilic derivative is prepared in situ during the formation of linear high polymers at elevated temperatures. Brown (252,260) prepared several thermoplastic materials by reaction of anilides and ureas with trimeric phosphonitrilic chloride at 200 °C. Not all of the chloride was removed by the reaction; the postulated linear structure of the acetanilide product is

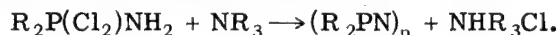
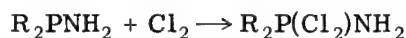


The reaction of primary amines with cyclic phosphonitrilic chlorides at 350 °C for 1 hour under a pressure of 0.1 torr produced a pale yellow, hard, brittle, glassy solid when *n*-butylamine was used (261). The product was reported to be insoluble in water and organic solvents, and to be resistant to the action of acids and alkalis. The high temperatures necessary to form the polymers and the residual halide in the products are factors which do not make these materials suitable for dental use.

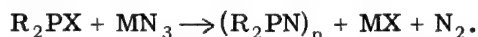
The third method for preparation of high-polymer phosphonitrilic derivatives involves the proper choice of starting materials and reaction conditions so that the desired polymer is formed directly; lower-molecular-weight polymers and products with residual halides are avoided by this method. Extension of the classical phosphonitrilic halide synthesis of phosphorus pentachloride with ammonium chloride (Reaction 1 below) to the use of dialkyl- or diaryltrichlorophosphine has been useful in the preparation of cyclic trimeric and tetrameric phosphonitrilic alkyl (262,263) or aryl (264,265) derivatives (Reaction 2).



Although only 50 to 60 percent of the isolated products are trimeric and tetrameric derivatives, the remaining residues have not been thoroughly studied as a possible source of the higher homologs. The halogenation of trivalent phosphorus amines followed by dehydrohalogenation produces predominantly cyclic symmetrically substituted phosphonitrilic homologs which are of low molecular weight (266):



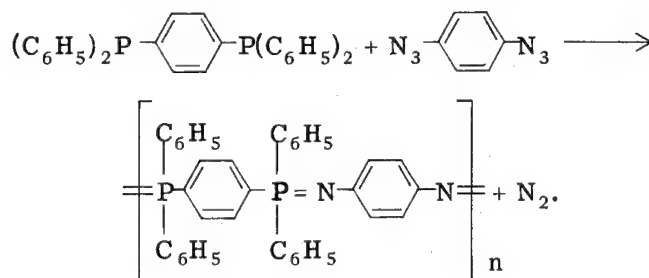
The most promising method of derivative preparation is that reported by Herring (267) which involves the reaction of a trivalent phosphorus halide with an alkali metal azide, usually lithium azide:



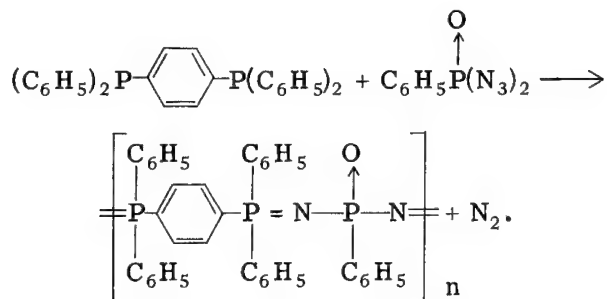
A distinguishing feature of the synthesis is that the bulk of the product is highly polymeric with only traces of trimer and tetramer isolated. The diphenyl derivative,  $[(\text{C}_6\text{H}_5)_2\text{PN}]_n$ , prepared by the azide method was a white powder which resisted the action of water and 0.1N sodium hydroxide (267). Herring et al. (268) have postulated a mechanism for the formation of the trimer, tetramer, and poly(phosphonitrilic)diphenyl derivatives by the azide method.

Another interesting material prepared by the azide method is the bis(trifluoromethyl)-phosphonitrile polymer,  $[(\text{CF}_3)_2\text{PN}]_n$  (269-272). The white waxy material, melting range 90 to 94°C, apparently was unaffected by refluxing sulfuric, nitric, or perchloric acid, but was partially hydrolyzed by treatment with 10% sodium hydroxide solution. Unfortunately, the intermediate azide,  $(\text{CF}_3)_2\text{PN}_3$ , explodes violently even at liquid-nitrogen temperatures without apparent reason. Since new procedures of preparation may lead to the same product by a route that would be suitable for dental manipulative requirements, the currently used preparative procedure should not be made the sole screening requirement if the material has desirable properties.

Herring (273,274) extended the azide procedure and prepared the first linear polymer in which an organic moiety regularly alternates with the phosphonitrile group,  $-\text{P}=\text{N}-$ , through which the conjugated unsaturation can be transmitted:

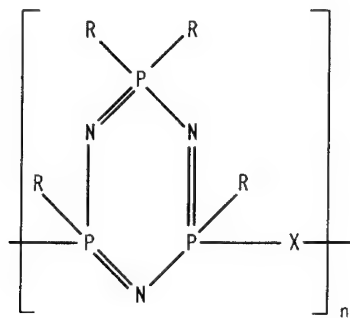


Baldwin and Billig (275) have extended the reaction to prepare "phosphorane polymers" of low molecular weight ( $n \approx 3$  to 4):



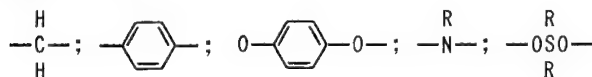
The hydrolytic stability was not reported; but based on several "model" compounds, it is predicted that the materials would be resistant to water, acids, and bases. Polymers of the above structure illustrate the use of organic radicals, in this case p-phenylene, to bridge between an otherwise unstable bond, phosphorus-phosphorus.

Conceivably two methods can be used to form polymers from cyclic phosphonitriles. First, as already discussed, the linear polymers can be formed by ring opening and reorganization of the structural units. Factors which limit the usefulness of the linear phosphonitrilic polymers are: (a) low-molecular-weight products, oils and liquids rather than high-molecular-weight solids; (b) hydrolytic instability; and (c) thermal degradation to the more stable cyclic compounds. A second method of polymer synthesis starts with the cyclic phosphonitrilic compounds and uses the reaction of active groups on the ring phosphorus with a difunctional linking group, for example hydroquinone, to form polymers with cyclic trimeric or tetrameric phosphonitrile moieties in the polymer backbone. As found for cyclic boron compounds, organic or inorganic groups may be used to link the phosphorus-nitrogen ring systems:



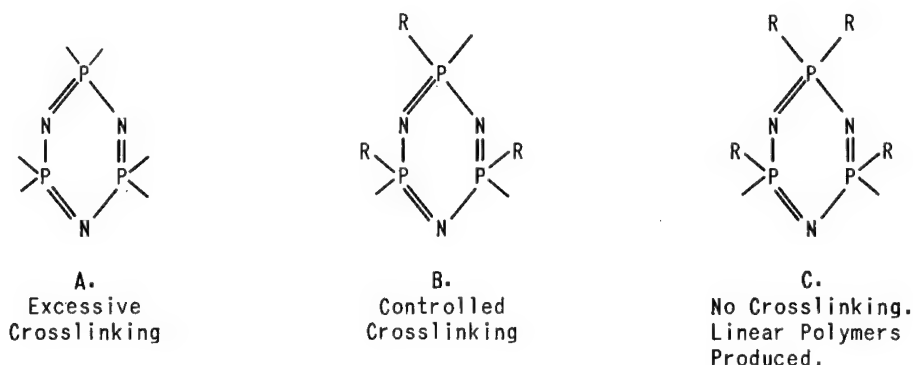
where R is a blocking group, for examples:  $\text{C}_6\text{H}_5\text{---}$ ;  $\text{---N}(\text{CH}_3)_2$   
 $\text{CH}_3\text{CH}_2\text{---}$ ;  $\text{---OC}_2\text{H}_5$ ;  $\text{---OC}_6\text{H}_5$

X is an organic or inorganic difunctional group, for examples:



The groups used to link ring systems together have been most successful when a portion of the bridge between rings is organic. Although not strictly within our definition of an inorganic polymer, the polymers with organic linking groups show promise as dental materials and warrant further investigation and evaluation.

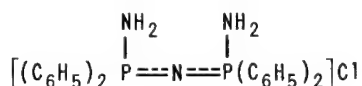
The cyclic phosphonitrilic halides possess multifunctionality; for example, trimeric phosphonitrilic chloride is capable of hexafunctionality. The use of such a group in a polymer backbone would result in highly crosslinked, rigid, intractable polymers. To reduce the multifunctionality of a compound, chemically stable blocking groups may be substituted in controlled numbers at reactive sites; the remaining active sites may act as points for linking two polymer moieties together. For example, the functionality of trimeric phosphonitrilic chloride,  $[\text{Cl}_6\text{P}_3\text{N}_3]$ , has been limited by controlled substitution of ring chlorine atoms by groups such as phenyl, phenoxy, alkoxy, and dialkylamino; the controlled substitutions have been the subject of several investigations. Three examples of linking  $\text{P}_3\text{N}_3$  rings through active points are



If only two functional positions remain on the ring, a linear polymer would form by linking the rings together (C). Controlled crosslinking can also be achieved during polymer formation by incorporating cyclic compounds of different functionality.

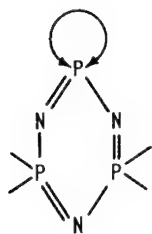
Garner and Klender (276-278), for example, reduced the trimeric phosphonitrilic chloride functionality to only two chlorine atoms per  $\text{P}_3\text{N}_3$  ring unit by using a mixture of phenoxy and ethoxy groups,  $[\text{Cl}_2(\text{C}_2\text{H}_5\text{O})_2(\text{C}_6\text{H}_5\text{O})_2\text{P}_3\text{N}_3]$ . On heating, a pre-polymer,  $\text{Cl}_{1.25}(\text{C}_2\text{H}_5\text{O})_{1.25}(\text{C}_6\text{H}_5\text{O})_{3.5}\text{P}_3\text{N}_3$ , was isolated which was cured at  $350^\circ\text{C}$  to a clear, hard, crosslinked resin without forming acidic by-products; brittleness of the polymer was attributed to the presence of phosphorus-oxygen-phosphorus bonds. The curing reaction is also reported to involve a sort of internal Friedel-Crafts reaction between phenyl rings of the phenoxy groups and the phosphorus-chlorine bond to give a  $\text{P}-\text{O}-\text{C}_6\text{H}_5$  linkage between  $\text{P}_3\text{N}_3$  rings rather than  $\text{P}-\text{O}-\text{P}$  linkages (276). Although the hydrolytic stability was not reported, the presence of the phosphorus-oxygen-phosphorus bonds in the polymer would make such materials susceptible to acid or base attack as noted in earlier sections.

Herring and Douglas (279-282) have reported a unique method of preparing substituted phosphonitriles which can be used to prepare polymeric materials through limited active positions on  $\text{P}_3\text{N}_3$  and  $\text{P}_4\text{N}_4$  rings. Ring closure reactions between bis(aminodiphenyl-phosphorane) chloride (283)

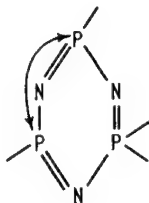


and pentavalent phosphorus halides, for example  $\text{PCl}_5$ ,  $\text{R}_2\text{PCl}_4$ , or  $\text{R}_2\text{PCl}_3$ , produce difunctional, monofunctional, and nonfunctional trimeric and tetrameric phenyl derivatives, respectively. Links between  $\text{P}_3\text{N}_3$  rings through organic groups, but using the above methods of reducing functionality, is promising for synthesis of useful dental materials.

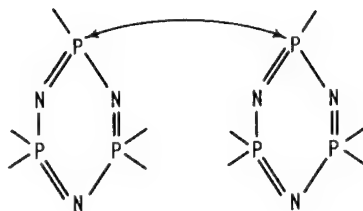
The difunctionality of the phosphorus atoms in the phosphonitrilic ring introduces a complication not encountered with borazole. A difunctional nucleophilic reagent must compete for positions on the same phosphorus atom (A), on two phosphorus atoms in the same ring (B), or on two phosphorus atoms in different rings (C):



A.



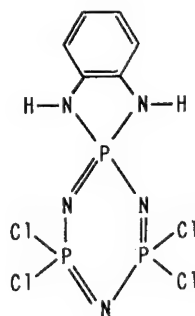
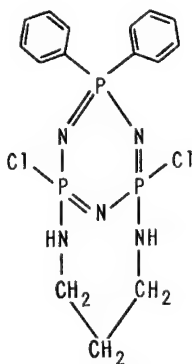
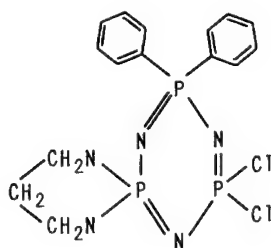
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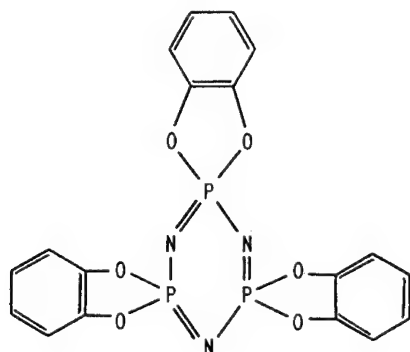
C.

The nature of the nucleophilic reagent will be expected to influence the positions favored. Phenyl substituents tend to activate the remaining chlorine on the same phosphorus, and multiple phenyl additions proceed geminally. Dimethylamino groups and phenoxy groups, however, deactivate the remaining chlorine on a substituted phosphorus, and multiple additions proceed nongeminally (237,238,241). Desirable polymers with  $P_3N_3$  rings in the polymer structure should be realized by the combination of proper monofunctional blocking groups and difunctional nucleophilic reagents.

Complications arise if proper blocking groups are not provided to prevent intra-ring substitutions. Becke-Goehring and Boppel (284) and Bode et al. (285) report diamine intra-ring substitutions that successfully compete with inter-ring substitutions which are desired for high polymer formation:



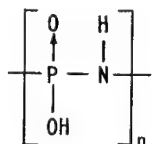
However, it is reported that phosphonitrilic chloride derivatives react with aliphatic diamines to produce thermoplastic resins; the resins were suggested for use as flame-retardant coatings and as adhesives for wood, glass, and cellulose (286). Similarly, certain diols favor intra-ring substitution; the reaction of phosphonitrilic chlorides with catechol in the presence of triethylamine formed the o-dioxyphenylene derivative with both oxygens on the same phosphorus (258,259,287):



The white crystalline solid, which forms inclusion compounds, produced low-molecular-weight vitreous materials on heating above its melting point; however, readily hydrolyzable chlorines were still contained in crosslinked networks between rings (259).

The reaction of diols has resulted in materials which should be further evaluated as dental materials. In general, the polymers are prepared by treating trimeric or tetrameric phosphonitrilic chlorides with a diol in the presence of a hydrogen chloride acceptor (287-293). Examples of recent investigations include the following diols: hydroquinone (277,278,294,295), catechol (259,274,296), phloroglucinol, pyrogallol, and resorcinol (294,295). The reported properties of the resins generally include little information of the hydrolytic stability.

Zhivukhin et al. (297) have investigated the use of diphenylsilanediol,  $(C_6H_5)_2Si(OH)_2$ , in place of the organic diols; the efforts to form copolymeric products with trimeric phosphonitrilic chloride have been unsuccessful. Poly(diphenylsiloxane), which had a different drop-point than materials polymerized without the presence of phosphonitrilic halide, and poly(metaphosphimic) acid

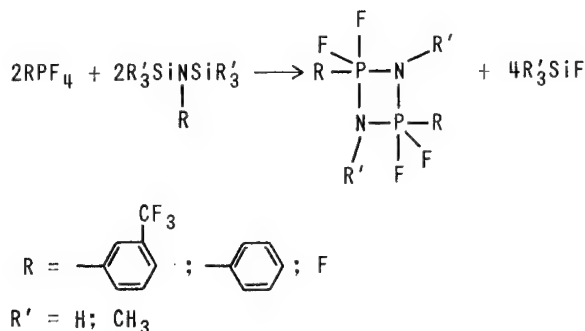


were obtained. The presence of quinoline in the reaction mixture caused the production of a yellow, pasty solid which contained 1.5% silicon and had a large number of phosphorus-oxygen-phosphorus bonds. After exposure to the air, the hydrolyzed polymers were insoluble in polar solvents. Using "oily-phosphonitrilic oligomers" (degree of polymerization about 12) with diphenylsilanediol, a 90 percent yield of a light yellow to brown polymeric material was isolated. The solid, having a molecular weight under 2500, was completely soluble in chloroform, benzene, and other aromatic hydrocarbons, but insoluble in alcohols and ketones. The polymer possessed considerable hydrolytic stability, although it was gradually decomposed in 0.5N potassium hydroxide.

The wealth of information pertaining to the phosphonitrilic system indicates a possibility of finding useful dental materials in this system. The most likely materials appear to be those containing cyclic phosphonitrilic systems, with limited functionality, linked together by a difunctional radical, for example organic diol, diamine, or siloxanediol. The use of the most stable form of an inorganic system to form the polymer backbone is more promising than forcing the repeating units into an unstable configuration. The use of organic radicals to link together otherwise unstable bonds is again illustrated by the phosphorus-nitrogen system considered.

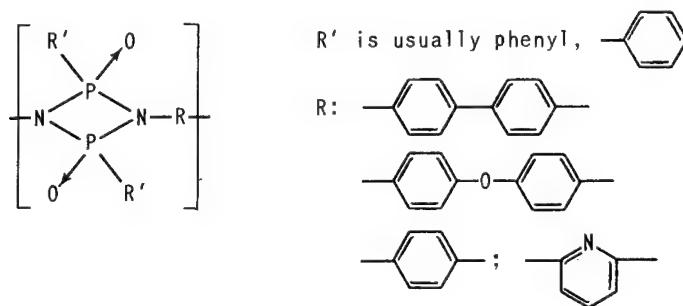


Other cyclic phosphorus-nitrogen systems have been investigated either as intermediates in the preparation of linear phosphonitriles or as new ring moieties for polymer backbones. Moran et al. (251) and Schmutzler (298) studied a cyclic system which was prepared by a novel reaction of broad scope; the reaction of a disilazane with a phosphorus(V) fluoride yields fluorosilane and an N-alkyl-P-aryl-difluorophosphine imide dimer,  $(\text{RF}_2\text{PNR}')_2$ , which exhibits excellent stability toward aqueous hydrolysis:



The cyclic difunctional units linked together by difunctional groups may lead to materials suitable for dental applications.

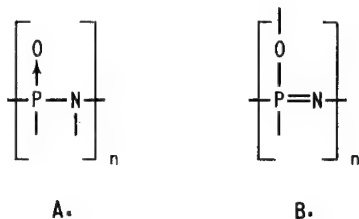
A related cyclic phosphorus-nitrogen structure was prepared by Nielsen et al. (299,300) by the reaction of phosphorus(V) imides with diamines; the products contain four-membered rings linked through a bridging aromatic difunctional group:



Although hydrolytic stability was not reported, the 1,3,2,4-diaza-phosphetidine 2,4-dioxides exhibit excellent adhesion to glass and metals—a property that indicates the structures may be useful as adhesive restorative dental materials.

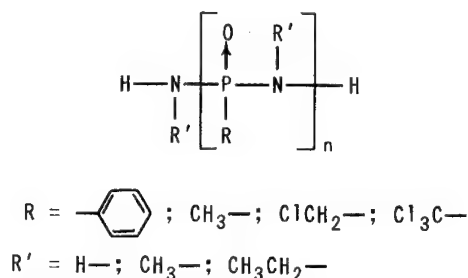
Another class of phosphorus polymers which may be applicable as dental materials contain a phosphorus-nitrogen backbone with one semipolar oxygen atom ( $\text{P}=\text{O}$  or  $\text{P}-\text{O}$ ) attached to the phosphorus (301). The system may be considered an analog of the completely inorganic phosphorus oxynitride, PON, a white, amorphous, chemically stable powder. Phosphorus oxynitride is insoluble in all usual solvents and is not attacked by aqueous acids or alkalis; however, it is hydrolyzed by water or moist air at a temperature of  $200^\circ\text{C}$ . A layer of phosphoric acid rapidly forms on the surface under these somewhat extreme conditions. Phosphorus oxynitride is also nonvolatile and heat resistant; it melts above  $1000^\circ\text{C}$  to form a glass, but it slowly decomposes above  $750^\circ\text{C}$  at very low pressures. These characteristics suggested the use of phosphorus oxynitride in heat-resistant compositions (302).

Although extensive crosslinking is indicated, the exact structure of phosphorus oxy-nitride is in doubt, and several proposed structures appear consistent with experimental data (301). Two classes of "PON" polymers, with substituent groups for chain branching and regulation of crosslinking, contain phosphorus and nitrogen linked by single covalent bonds (A) or linked by alternate single and double bonds (B):

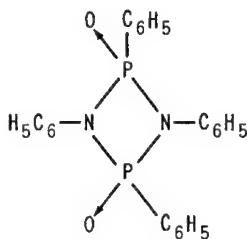


Polymers containing the second structure (B) were briefly discussed with the phosphonitrilic system; the phosphorus-oxygen-phosphorus bond is a hydrolytically weak bond and its presence in materials for dental applications is not desirable.

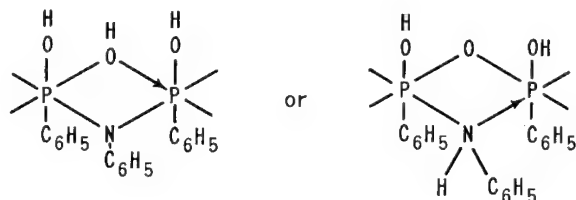
Polymers reported to have the first type structure (A) above were prepared by thermal de-amination of phosphonic diamides which have at least one hydrogen on the amide nitrogen,  $\text{RP(O)(NR'H)}_2$  (303,304). The properties of the crystalline polymers formed from phenylphosphonic diamide,  $\text{C}_6\text{H}_5\text{P(O)(NH}_2)_2$ , depend on the temperature used in the de-amination polycondensation (303). A water-insoluble product was formed above  $280^\circ\text{C}$ ; a viscous mass which solidified to a porous, brittle, nearly colorless glass was produced at  $400^\circ\text{C}$  or above. Although the means of molecular weight measurement were restricted, low-molecular-weight products were indicated. The polymer in which  $\text{R} = \text{---}\text{C}_6\text{H}_5\text{---}$  and  $\text{R}' = \text{CH}_3\text{---}$



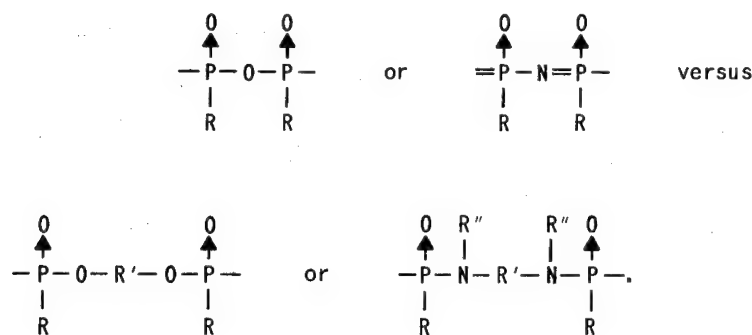
was isolated as an amber-colored, glassy material. The polymer was soluble in chloroform and in methanol, insoluble in benzene, and appeared to react with a water-methanol mixture. Attempts to prepare the N-phenyl polymer ( $\text{R} = \text{R}' = \text{---}\text{C}_6\text{H}_5\text{---}$ ) resulted in the formation of a cyclic dimer of phenylphosphonic imidoanilide (303):



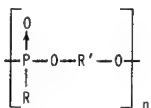
Polymerizations attempted in the presence of water produced products which could not be dehydrated; the compounds contained one water molecule per phosphorus atom. Phosphorus-nitrogen ring formation would be prevented if the postulated six-coordinated phosphorus atoms in the polymer backbone were formed (301):



The Class 3 polymers of phosphorus containing phosphorus-oxygen-silicon polymer backbone units were discussed in the silicon section. Although polymers containing carbon in the backbone were not intended to be included in this report, Class 3 phosphorus polymers containing carbon will be briefly discussed. The reason is that carbon in organic moieties can be used to stabilize unstable units by linking of the phosphorus-oxygen or phosphorus-nitrogen through a difunctional organic group, for example



A series of materials, suggested as flame-resistant polymers, will illustrate the Class 3 phosphorus-oxygen-carbon polymers (304):

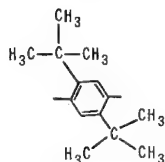
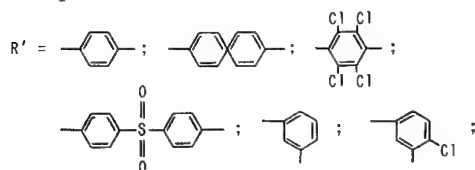


R = C<sub>6</sub>H<sub>5</sub>;

CH<sub>3</sub>—; CH<sub>3</sub>CH<sub>2</sub>— (hard and tough materials)

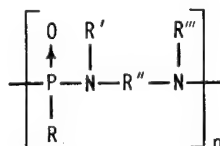
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>— (rubbery materials)

ClCH<sub>2</sub>—

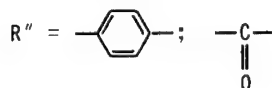
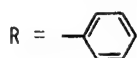
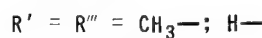


Although the presence of moisture was harmful during the polycondensation reactions, it was implied that the reported products were hydrolytically stable. Copolymerizations and trans-esterifications were procedures used to alter the nature of the brittle products. Further evaluation of the reported products, as well as preparation of new materials, may lead to polymers suitable for dental materials; however, toxicity may be a problem.

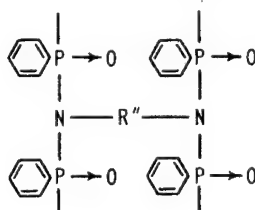
The phosphorus-nitrogen-carbon polymers are more complex than the oxygen analogs because of the three-coordinated nitrogen atom. A general formula of these Class 3 compounds is



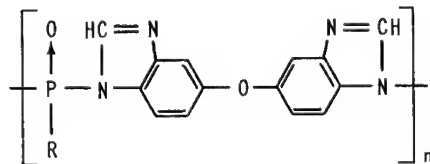
In general,



Several polymers were reported to have excellent adhesion to glass and stainless steel. The brittle polymer in which  $\text{R} = -\text{C}_6\text{H}_5$ ,  $\text{R}' = -\text{CH}_3$ , and  $\text{R}'' = \text{---} \text{C}_6\text{H}_4 \text{---}$  is insoluble in water or hexane but soluble in methyl alcohol, ethyl alcohol, chloroform, and pyridine (300). When  $\text{R} = -\text{C}_6\text{H}_5$ ,  $\text{R}' = -\text{H}$ , and  $\text{R}'' = \text{C}=\text{O}$ , the polymer is insoluble in acetone and in water, but partially soluble in dimethyl formamide (303). Gutmann et al. (305) prepared solid materials by heating under reduced pressures polymers in which  $\text{R} = -\text{C}_6\text{H}_5$  and  $\text{R}' = -\text{H}$ . The structures of the glassy products are represented as crosslinked chains:

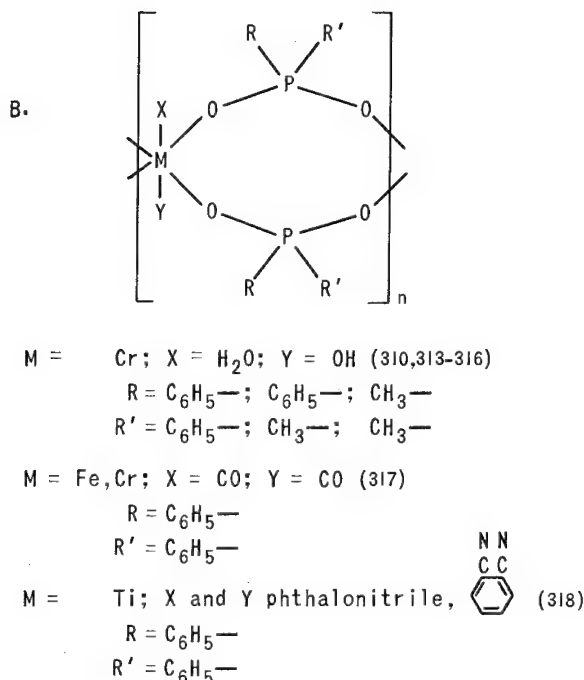
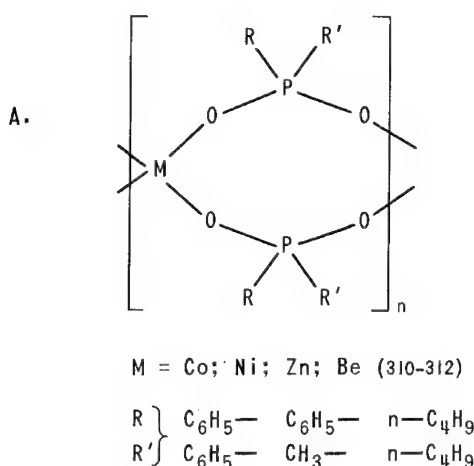


However, Parts, Nielsen, and Miller note that a completely condensed product would have identical compositions to the reported diphosphetidine polymer prepared from the same diamine (299). Johns and Nielsen (300) have also reported a rather unique linking group of the benzimidazole type:



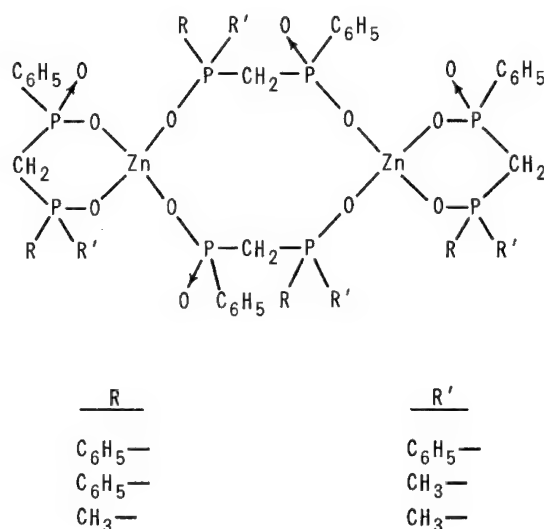
The examples presented for the phosphorus-nitrogen-carbon Class 3 polymers lack an indication as to the stability of the materials toward attack by water, acid, or base. Even if the polymers have chemical stability compatible with their use as dental materials, the toxicity of the materials may prevent their use.

Several additional Class 3 polymers which contain elements other than carbon in the phosphorus-oxygen-element\* polymer backbone have been reported; however, the chemical stability toward water, acids, and bases is such that the polymers do not appear to be suitable for dental materials. A new Class 3 polymer system receiving attention recently consists of a double-bridge repeating unit of phosphorus-oxygen-metal (306-309):



\* Elements which have been reported to form P-O-M polymers are beryllium, boron, aluminum, arsenic, titanium, chromium, cobalt, nickel, zinc, and molybdenum.

Molecular weight determinations of the double-bridge phosphinate polymers indicate values in the range of 10,000. Observed viscosity changes in polymer-chloroform solutions are attributed to an increase in polymer chain length (307). The reported polymers range from intractable, infusible solids to low-melting solids soluble in most common organic solvents. The common disadvantages noted for most inorganic polymers are also noted for these polymers, for examples, low molecular weight and brittleness. A preliminary report (319) indicates that the materials have good hydrolytic stability, but they appear to be attacked by aqueous sodium hydroxide. Polymers containing zinc (structure A above) dissolved in 5% sodium hydroxide at room temperature and were reprecipitated in polymeric form by neutralization. The chromium polymers (structure B) were destroyed by boiling 5% sodium hydroxide. Attack by 5% hydrochloric acid was reported to be only slight for the zinc and chromium polymers. Other six-coordinated metals, linking groups, organic groups on the phosphorus, and chelating groups for metals are currently being studied. Attempts to make higher-molecular-weight polymers by use of phosphinylmethylphosphinates were unsuccessful as a result of formation of low-molecular-weight compounds (320) of the type



The double-bridged phosphinate polymers reported to date do not exhibit properties that are conducive to good dental materials.

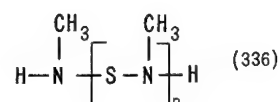
## 2. Arsenic and Antimony Polymers

Although the toxicity of polymers considered for dental materials must be thoroughly investigated, the known highly toxic nature of arsenic and antimony compounds, as well as the lack of distinct advantages over analogous phosphorus polymers (321-323), exclude the arsenic and antimony polymers from consideration as restorative materials in the human body. Hobin (324) has summarized the field of organo-arsenical polymers and should be consulted for pertinent references to Class 1 and 2 arsenic polymers.

A possible future investigation may involve controlled liberation of small quantities of bactericides into the mouth or tooth via the dental restorative material analogous to antifouling paints on ships. For controlled liberation of toxic materials, the Class 3 polymers of arsenic and antimony may prove applicable. Low-molecular-weight Class 3 polymers have been reported with the following backbone units: silicon-oxygen-arsenic (325,326), silicon-oxygen-antimony (327), and tin-oxygen-arsenic (328,329).

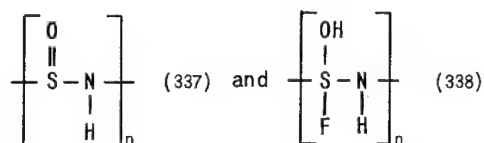
## D. Group VI: Sulfur

Class 2 sulfur polymers, which have some suitable properties for use as dental materials, contain either sulfur-carbon or sulfur-nitrogen linkages. The rubber-like thiokols,  $[C_xH_{2x}S_y]_n$ , are industrially important, but a discussion of these compounds is beyond the scope of this report. Berenbaum and Panek (330) recently reviewed the chemistry and applications of thiokols. Polymers which contain sulfur-nitrogen chain units exemplify the use of appended groups or atoms to the polymer backbone to change the polymer properties. The brass-colored, semiconducting polymer  $[SN]_n$  is slowly attacked by dilute alkali and rapidly hydrolyzed by concentrated alkali (331-335). Unfortunately, the intermediate  $S_2N_2$  used in the formation of  $[SN]_n$  detonates on heating above  $30^\circ\text{C}$  or on rubbing. A polymer having an alkyl group appended to the nitrogen has been reported by Stone and Nielsen:

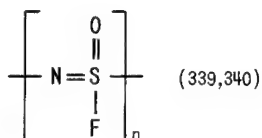


The gummy product is capable of being stretched into long threads; but when stretched rapidly it fractures, and when struck sharply the material shatters (336). The solubility of this polymer in benzene, chloroform, and pyridine suggests a small amount of cross-linking. However, the polymer is unstable and decomposes slowly on standing and violently at  $90$  to  $100^\circ\text{C}$ .

Becke-Goehring reported the polymers

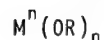


which are readily hydrolyzed by water. The tough elastic polymer

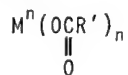


is not affected by cold aqueous ammonia, cold water, or 6% sulfuric acid at  $100^\circ\text{C}$ ; however, the sulfuric-fluorine bond is readily attacked by nitrogen bases at elevated temperatures. The presence of fluorine in the polymer presents an interesting possibility: a dental restorative material that could continually supply fluorine in the mouth to arrest tooth decay.

## E. Polymers of Metals that Form Alkoxides or Carboxylates



A.

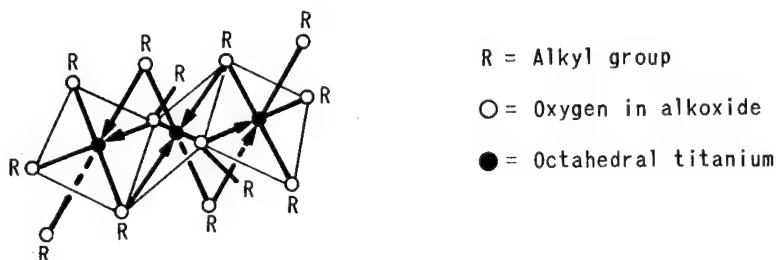


B.

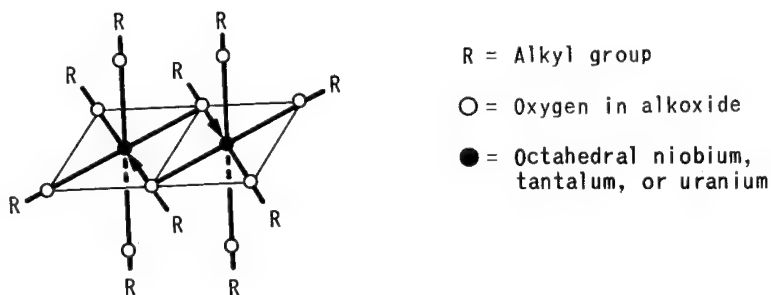
Metal alkoxides (A) and carboxylates (B) were mentioned in the silicon section (II, B1) as intermediates in the formation of poly(metallosiloxanes). Metal acetates have found some industrial uses (341, 342), and metal

alkoxides are enjoying a rapid increase in industrial importance (343); titanium alkoxides have been especially useful (344,345). The major alkoxide applications include (a) components in heat-resistant paints, (b) water repellents, (c) paint driers and modifiers, (d) polymerization catalysts, and (e) various coating systems (343,346,347).

By expanding the coordination number of the metal by polymerization rather than by coordination with another ligand, the metal alkoxides form the smallest unit in which all of the metal atoms attain their maximum coordination number. Thus, the alkoxides tend to adopt that polymeric structure which contains the maximum number of alkoxide bridges between adjacent metal atoms. For example, the smallest possible titanium alkoxide polymer consistent with the above structural principle is the trimer (348),  $[\text{Ti}(\text{OR})_4]_3$ :

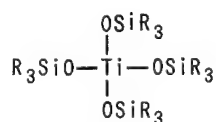


The degree of polymerization is found to be dependent on the metal involved and the extent of branching present in the alkoxide group. Thus, the alkoxides of niobium and tantalum have not been reported in compounds in which dimerization is exceeded:



Unlike the trimeric titanium ethoxide, titanium isopropoxide is monomeric.

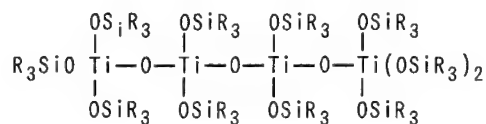
Most of the metal alkoxides are readily hydrolyzed in the presence of excess water to give the metal hydroxide and ultimately the metal oxide. Bradley (343) has summarized the present knowledge concerning the hydrolysis of titanium alkoxides. In brief, the rapidity and completeness of the hydrolysis depends on the alkyl group size; the hydrolysis is slower and less complete when large alkyl groups are used than when small groups are used. Unlike silicon, titanium does not form hydrolytically stable carbon-metal bonds; the same is true for other metals that form alkoxides, for example, zirconium and aluminum. Trialkyl- and triarylsilanol groups,  $\text{R}_3\text{SiO}$ , have been mentioned earlier as effective blocking or framing groups for elements which do not form stable carbon-metal bonds. Whereas titanium ethoxide is rapidly hydrolyzed by water, the rate of hydrolysis is relatively slow for tetrakis(trialkylsiloxy)titanium (349-351):





Tetrakis(triphenylsiloxy)titanium resists attack by hot concentrated hydrochloric acid and hot 0.1N sodium hydroxide (352); however, the trialkylsiloxy derivatives are readily and quantitatively decomposed to hexaalkyldisiloxane by hot dilute sodium hydroxide. Much of the inert character of the triarylsiloxy derivatives may be due to their resistance to wetting under the conditions studied.

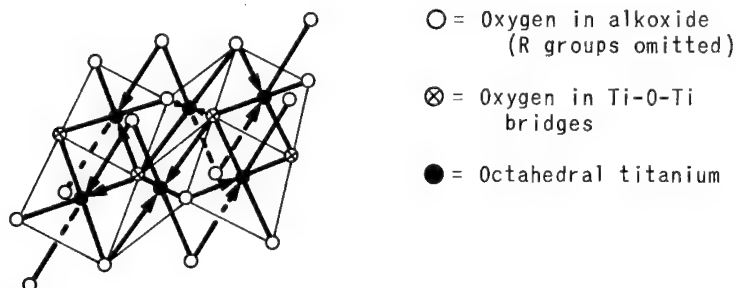
The hydrolysis of tetrakis(triaryl- or trialkylsiloxy)titanium in the presence of catalysts forms low-molecular-weight poly(titanoxanes) (347):



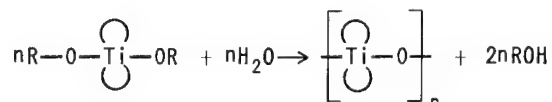
Bradley et al. (343,353,354) studied the structural aspects of the hydrolysis of titanium alkoxides and reported the reaction to be a stepwise one involving the formation of an infinite trilinear polymer having the ultimate formula  $[\text{Ti}_3\text{O}_4(\text{OR})_4]_\infty$ . The intermediates formed during the condensation-polymerization have the general formula

$$[\text{Ti}_{3(x+1)}\text{O}_{4x}(\text{OR})_{4(x+3)}] \text{ where } x = 0, 1, 2, 3, \dots \infty.$$

For the methyl derivatives, compounds isolated were  $\text{Ti}_6\text{O}_4(\text{OCH}_3)_{16}$  where  $x = 1$



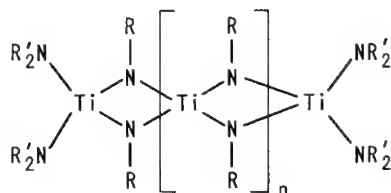
and  $\text{Ti}_{12}\text{O}_{12}(\text{OCH}_3)_{24}$ ,  $x = 3$ . Typical of most condensed polymers isolated from a metal alkoxide, the titanate films that form from solvent evaporation are initially transparent on exposure to moist air; however, in time the film becomes opaque and brittle due to the formation of titanium dioxide. The rate of hydrolysis decreases as the degree of polymerization increases (355). Attempts to prepare polymers that would be less readily hydrolyzed have been reported; uses of chelate blocking groups with the more reactive alkoxide groups for condensation have been investigated:



Acetylacetone (356), 8-quinolinol (357) and dibenzoylmethane (357) are several chelating compounds studied; however, the resulting condensation products were still susceptible to hydrolysis.

Although the polymeric products which are obtained from the hydrolysis of metal alkoxides do not have acceptable properties for dental materials, the use of metal alkoxides and carboxylates in the study of the metal oxide formation or polymer formation in solution may be very important in the search for dental materials. The room-temperature polycondensations that take place with the formation of nontoxic by-products could be the basis of polymerizations that can be carried out in a tooth cavity. The solution polymerization of the alkoxides should be studied in the same manner as polyelectrolytes (358,359,360). The goal of the hydrolysis-polymerization investigation would be means by which high-molecular-weight inorganic materials can be formed. We used as our examples in this section the more important titanium compounds; suggested investigations could be extended to other metal alkoxides, for example, zirconium (361,362) and vanadium (363,364).

Bradley et al. (365,366) have reported a series of double-bridged Class 2 polymers containing titanium-nitrogen units in the chain:



As expected, the resulting materials containing a postulated four-coordinated titanium are susceptible to attack by water, acids, and bases; however, the materials prepared did show an increased hydrolytic stability as the molecular weight of the alkyl group on the nitrogen increased. For dental applications, the organic chemistry of titanium (367) does not suggest titanium polymeric systems other than the Class 2 titanium-oxygen polymers.

### III. CONCLUSIONS AND RECOMMENDATIONS

The lack of a uniform polymer evaluation procedure has prevented a totally effective screening of the inorganic polymer literature for useful dental materials. Of the nine requirements set down in section IB as criteria for suitable dental adhesive restorative materials, only three could be used for screening purposes: toxicity, hydrolytic stability, and method of preparation. Furthermore, the hydrolytic stability reported in the literature may be misleading; overall polymer degradation and chain-end initiated reactions are not differentiated.

Although the repeating unit,  $\text{[-M-L-]}_n$ , may be useful to classify various polymers, it fails to recognize the groups which so importantly terminate the polymer chains. Extensive investigations of organic and inorganic polymer systems have shown that thermal degradative reactions are frequently initiated at the chain ends; a similar degradative process might be applicable to hydrolytic attack. Inorganic polymers that are investigated for use as dental materials should be evaluated with various end groups; hydrolytically stable polymers may be formed by using hydrolytically stable end groups. The thermal and hydrolytic stabilities of a given inorganic polymer backbone will be more properly identified if a procedure of end-group variance is used in the investigation.

Although numerous proposals for future investigations are discussed throughout the report, only a few polymer systems (Table 6) are suggested for further evaluation as dental materials. Two polymer systems that are promising for dental applications are poly(organosiloxanes) (section IIB1) and poly(metallosiloxanes) (section IIB1). Many

Table 6  
Conclusions Concerning Inorganic-Polymer Systems,  $\{M-L\}_n$ , That Were  
Screened for Useful Dental Materials.

M	L					
	M	Oxygen	Nitrogen	Carbon	Other Elements	Class 3 Polymers
Group III B	4	4	1	1*	B-P: 1	B-O-Si: 2
Al		4	4			Al-O-Si: 4
Group IV, IV B Si	4	1;2;3	2			Si-O-Element: 3
Ge	4	4	4			
Sn	4	4	4			
Pb	4	4	4			
Group V, V B						P-N-C: 1 P-O-C: 1 P-O-Metals: 4
P	4	3;5	1			
As	4	4	4			4
Sb	4	4	4			4
Group VI S	4	4	3			
Other Metals Ti and other metals that form alkoxides or Carboxylates.		3;5	4			

1. Possible use as adhesive restorative dental materials
  2. Possible use as precoating materials
  3. Specialty uses in dental applications
  4. Not suitable for dental applications
  5. Long-range investigations may lead to useful information applicable to dental-material preparation
- \*Polymers containing the carborane units

silicon materials are readily available and could be systematically screened for dental applications now; the major producers of silicones—Dow Corning Corp., General Electric Co., and Union Carbide Corp.—should be excellent sources for the desired test materials. Other polymers that are promising as dental materials contain stable inorganic ring systems that are bridged by organic groups or that act as chain-branching moieties. Further investigations and evaluations are suggested for carborane polymers (section IIA1) and for polymers containing boron-phosphorus (section IIA1) and phosphorus-nitrogen (section IIC1) ring systems.

Since an unstable inorganic repeating unit generally shows an increased stability if an organic group is added between two such units, a thorough literature search is advisable for Class 2 and Class 3 polymers that contain carbon as the linking atoms in simple or complex groups. When complex organic groups are used as links between the inorganic portions of the polymer, the resulting Class 2 or Class 3 polymers are referred to as coordination polymers. The available information pertaining to coordination polymers generally consists of preparative methods, structures, magnetic properties of the coordinated metals, thermal stabilities, and possibly hydrolytic stabilities. Although the low-molecular-weight polymers may not be suitable for dental materials, a literature survey of the coordination polymers is deemed advisable at some future time because of the other dental applications that may be suggested by the survey.

As thorough as this report was intended to be, excellent polymers and polymer systems for dental materials may have been overlooked or eliminated from consideration. If this report stimulates the thoughts of others in the inorganic polymer field to recognize the omissions, and if new or known polymer systems are brought to light, it will have served its purpose. The intent of the report is to help evolve a radically new dental material and not to seek a stop-gap until a good dental restorative material is found.

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<p>A new adhesive restorative dental material must meet rigid requirements. These must be kept in mind in screening inorganic polymer systems reported in the literature; but since the available literature data are limited, only three requirements—toxicity, chemical stability, and ease of manipulation—were used in this evaluation.</p> <p>The problem was approached by considering polymers according to the group number of the elements contained in the polymer backbone. The inorganic polymers were in turn grouped into three classes: Class 1, polymers having only one element in the polymer backbone; Class 2, polymers having two different elements in the backbone; and Class 3, polymers having three or more different elements in the backbone.</p> <p>Inorganic polymer systems which appear most promising for use as dental materials are the Class 2 polymers containing linear silicon-oxygen backbones and Class 2 polymers containing boron-phosphorus or phosphorus-nitrogen ring systems as moieties in the backbone.</p>		



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